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FIELD SURVEILLANCE AND ENFORCEMENT GUIDE: WOOD PULPING INDUSTRY

S. Oglesby, et al

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FIELD SURVEILLANCE AND ENFORCEMENT GUIDE: WOOD PULPING INDUSTRY

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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This manual provides guidelines and background information for use by personnel of state and local air pollution control agencies in their surveillance and enforcement activities related to the major types of chemical pulp mills. The three major types of mills discussed are Kraft, Sulfite, and Neutral Sulfite Semi-Chemical (NSSC). For each type of mill, the process is described; the emissions, both gaseous and particulate, are characterized; and the types of applicable control equipment are delineated. Field enforcement inspection, reporting and enforcement procedures to be followed in each type of mill by control agency personnel are suggested.

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CHAPTER 1

INTRODUCTION

1.1 OBJECTIVES AND SCOPE

This manual provides guidelines and background information for use by personnel of state and local air pollution control agencies in their surveillance and enforcement activities related to the major types of chemical pulp mills. The three major types of mills discussed are Kraft, Sulfite, and Neutral Sulfite Semi-Chemical (NSSC). For each type of mill, the process is described; the emissions, both gaseous and particulate, are characterized; and the types of applicable control equipment are delineated. Field enforcement inspection, reporting and enforcement procedures to be followed in each type of mill by control agency personnel are suggested.

1.2 ROLE OF FIELD INSPECTION IN AN ENFORCEMENT PROGRAM

In any size control agency, it is necessary frequently to determine whether sources are in compliance with applicable regulations. This is the role of the field enforcement officer (FEO) in an air pollution control program. It is his responsibility, also, to carry out the functions of field inspection and enforcement.

One of the most important aspects of a control agency's enforcement activity is frequent and direct contact with the owners and operators of processes which emit air pollutants. Frequently, the FEO is the person to whom this task falls.

The FEO also may be involved in a variety of assignments depending on the size and organization of the agency and the regulations which are involved. In all approved state implementation plans, a permit or registration system is required. These programs assure that no new sources of air pollution are constructed, reconstructed, or altered without the knowledge of the agency. They also have provisions for the review of plans for construction or modification to insure that a proposed system is capable of operating in compliance with the regulations and makes it possible to develop and maintain emission inventories.

To insure that operating sources continue to comply with air pollution regulations, implementation plans provide for the audit of all sources periodically. The interval may range from once every six months to once every five years, although the usual time period is once each year. During these periodic checks, the FEO determines that the source is in compliance with permit requirements, reviews the emission data and inspects the site to insure good operating and maintenance practices.

Surveillance of a source may be conducted in a number of ways. The FEO may detect observable violations of the regulations from outside the source premises, by on-site inspections, and by emission measurements. The FEO has primary responsibility for the success of a source surveillance program even though he may not conduct the monitoring himself.

CHAPTER 2

THE CHEMICAL WOOD PULPING INDUSTRY

2.1 INTRODUCTION

The pulp and paper industry is the ninth largest manufacturing industry in the United States. This industry accounts for nearly four percent of the value of all manufacturing.

Although paper is one of the oldest manufacturing industries, it is an industry that is expanding faster than the general economy. Consumption of paper rises with increased affluence. The per capita consumption of paper in the U.S. is now over 550 pounds per year compared to about 412 pounds only 12 years ago. There are no signs that per capita consumption is leveling off.

The pulp and paper industry is comprised of three distinct segments: (1) pulp, (2) primary paper and paperboard (cardboard, etc.), and (3) converted paper and paperboard products.

Pulp--Most pulp is made by integrated companies and consumed captively without moving through the marketplace. About ten percent of the total pulp produced is, however, made by independent pulp producers without their own paper making facilities or by integrated companies producing surpluses for market. About three percent of all pulp produced is consumed outside the industry for such products as cellophane, rayon, cellulose esters and ethers, and their derivatives. Eighty percent of the pulp used for making paper comes from wood and 20 percent is made from waste paper or such fibers as cotton and bagasse.

Primary Paper and Paperboard--This segment of the industry produces paper, paperboard, and building paper and board. A portion of this production is sold directly to industrial users such as newspapers, book publishers, and printers, or to building and other users.

Converted Paper and Paperboard Products--About 70 percent of the primary paper production is further processed by paper converters into such products as containers, bags, sanitary tissue products, and stationery.

Wood pulp is prepared either mechanically or chemically. In the mechanical processes (groundwood, defibered and exploded) wood is shredded or separated by physical means. In the chemical processes--kraft, sulfite, neutral sulfite semi-chemical (NSSC), soda, and dissolving--wood is treated with chemical reagents which form soluble compounds with the noncellulosic materials, thus leaving residual cellulose. The NSSC process involves treating the wood first with a mild chemical and then mechanically separating the fibers.

Data are presented in Table 2-1 which show the number of mills and total mill capacities for the five chemical pulping processes. In Table 2-1, all capacities are based on air dried tons of pulp; annual capacities are based on operating at rated capacity for 350 days per year, allowing for normal maintenance and scheduled shutdowns. It is emphasized that these figures represent production capability and do not portray actual production data.

Three of the chemical wood pulping processes display a potential to cause air pollution. These are the kraft, sulfite, and NSSC processes. Collectively, these three processes account for about 80 percent of the total wood pulp produced in the United States.

To define the air pollution problem posed by the chemical wood pulping industry, it is necessary to establish the geographical distribution of existing production capacity and to identify trends which might cause a redistribution of production capacity in the future.

2.2 ECONOMIC POSITION

The United States pulp and paper industry includes more than 400 pulp mills of all types, mechanical and chemical. Estimates for 1967 indicate 37 companies, each with pulp and paper sales at the manufacturer's level of at least $100 million, accounted for $10.24 billion in sales, or 49 percent of the industry's total of $20.88 billion.

Table 2-2 shows the wood pulp production in 1971 for the ten leading pulp producing nations of the world (1). The other 60 pulp producing nations individually produced less than one million tons of pulp and collectively produced 14,441,000 tons of pulp in 1971. From these data, it can be determined that the U.S. and Canada produced 52 percent of the world's wood pulp in 1971. This massive capacity, coupled with the contiguous features of the U.S. and Canada, place these countries in a leading position in terms of production.

It is reported (2) that North American industry is planning to build 65 new pulp mills in the 1970's--39 in the U.S. and 26 in Canada. It seems reasonable to conclude, therefore, that the U.S. and Canada will remain the dominant nations in wood pulp production at least for the next two or three decades.

2.3 PRESENT GEOGRAPHIC DISTRIBUTION

A compilation of data on current wood pulping practice in the U.S. was made by searching available published reports, such as Lockwood's Directory of the Paper and Allied Trades, Post's Pulp and Paper Directory, and Southern Pulp and Paper Manufacturer's Southern

TABLE 2-1

SUMMARY - U.S.A.
CHEMICAL PULP MILL CAPACITIES (UNBLEACHED)
AS OF DECEMBER 31, 1971

Process	Number of Mills	Capacity* ADT/Day	Annual Capacity* Tons	1972 Production Tons
Kraft	128	93,600	32,800,000	30,250,000
Sulfite	44	6,650	2,324,000	2,150,000
NSSC	48	11,300	3,950,000	3,650,000
Dissolving	9	5,100	1,780,000	1,650,000
Soda	4	920	322,000	300,000
TOTALS	233	117,570	41,176,000	38,000,000

* These figures represent capacity and not actual production. ADT stands for air-dried tons of unbleached pulp per day; air-dried pulp contains 10 percent moisture.

TABLE 2-2

PRODUCTION OF TEN LEADING PULP PRODUCING NATIONS - 1971

Nation	Million Short Tons
United States	45.20
Canada	20.70
Sweden	9.20
Japan	9.00
Finland	7.72
USSR	6.78
Norway	2.59
Mainland China	2.30
France	1.77
West Germany	1.73

Mill Directory. Information originally tabulated included plant location, owner, pulping process employed, rated mill capacity, type of wood pulped, and age of original mill. These data were brought up to date based on in-house information, available NAPCA - NCASI reports, and communications with industry representatives. Using these data as a base, two maps have been prepared to illustrate geographically the distribution of chemical wood pulping mills throughout the United States. These maps are presented here as Figures 2-1 and 2-2.

2.4 FORECASTS

2.4.1 GROWTH AND PROCESS TRENDS

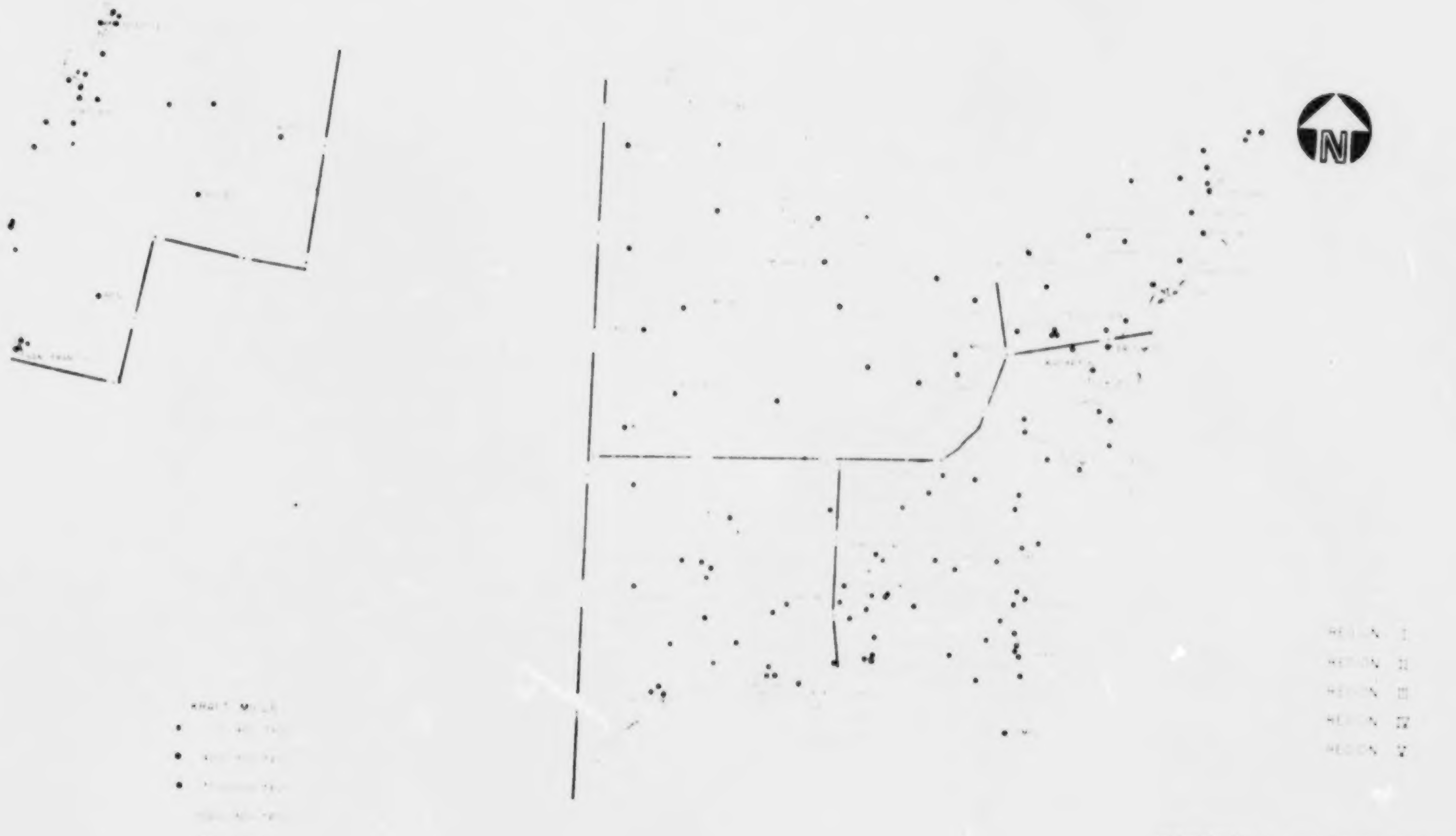
The United States and Canada produce more than 52 percent of the world's supply of pulp, with the U.S. in 1972 furnishing nearly 46 million short tons. Of this amount, 38 million tons were chemical pulp. Approximately 75 percent of this was produced by the kraft process, nine percent by the sulfite, and ten percent by neutral sulfite semichemical (NSSC).

A number of forecasts have been made which attempt to portray the future demand for wood pulp (all grades) in the United States. These forecasts range from a low of 61 million tons per year in 1985 as given by Forest Research Report No. 17, 1965 (3), to a high of 89 million tons per year in 1985 as given by Resources in America, 1963 (4). A middle of the road forecast has been made by the American Paper Institute. Based on these data, plus numerous other sources, H. W. Meakin of the J. E. Sirrine Company has projected chemical pulp production through 1985. These projections are reproduced here as Figure 2-3.

Viewed together, these data show that through 1985, the production of soda pulp and dissolving pulps will remain reasonably constant; sulfite pulp production will decrease slightly; NSSC production will nearly double, and kraft pulp will increase to approximately 2-1/2 times the 1968 amount.

In 1985, kraft and NSSC processes are expected to dominate chemical pulping in the United States. Kraft production is projected to account for about 85 percent of the chemical (about 70 percent of total wood pulp, all grades, production), and NSSC for about 9 percent of the total chemical pulp production. The total production of chemical pulp is expected to slightly more than double. Regional distribution of pulping capacity is expected to remain in the same relative proportions as it is today.

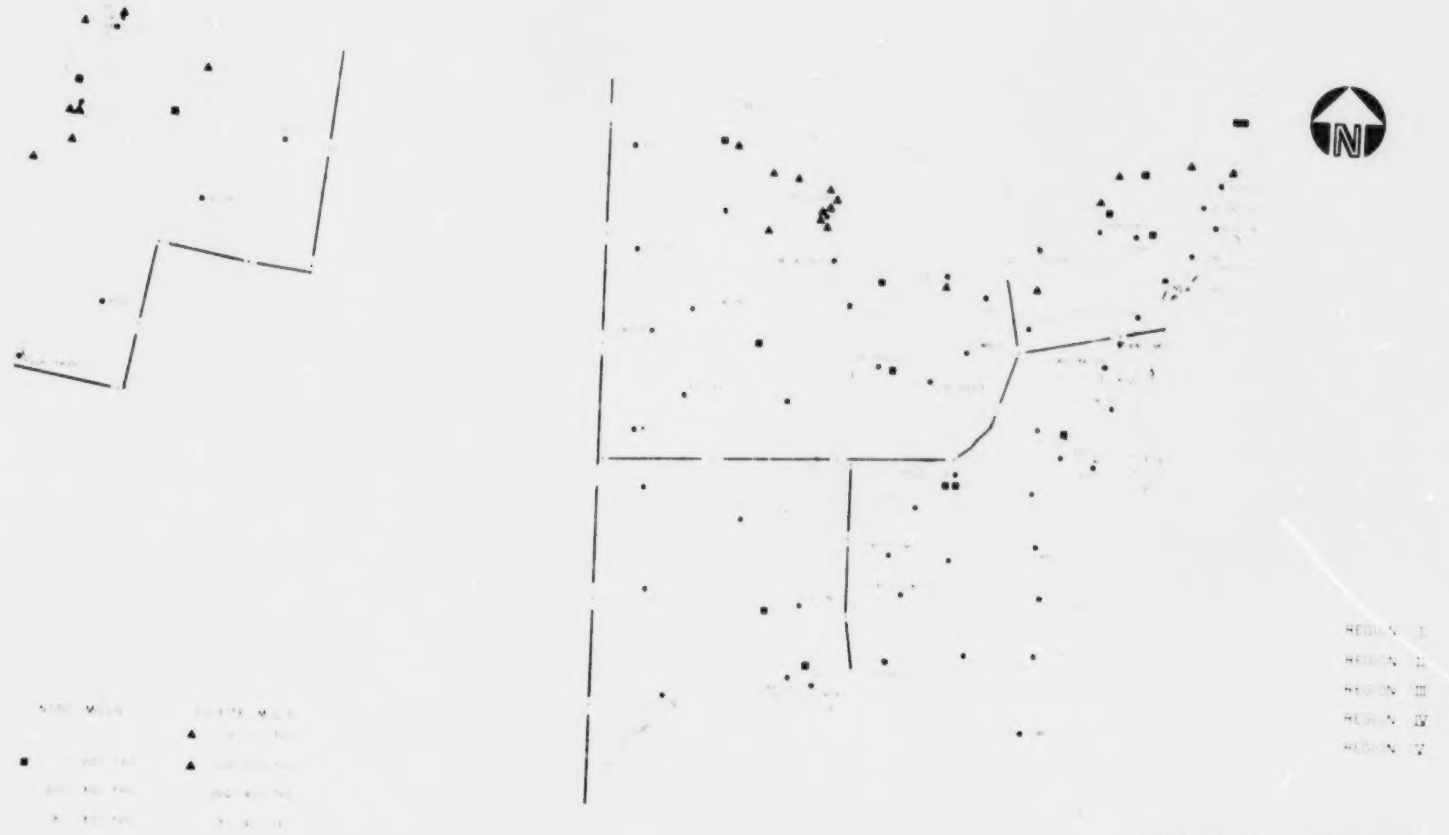
Table 2-3 has been included to summarize announced and estimated expansion and phasing-out operations through 1980.



KRAFT MILLS
REGION I
REGION II
REGION III
REGION IV
REGION V

REGIONAL DISTRIBUTION
OF KRAFT PULP MILLS
IN THE U. S.

FIGURE 2-1

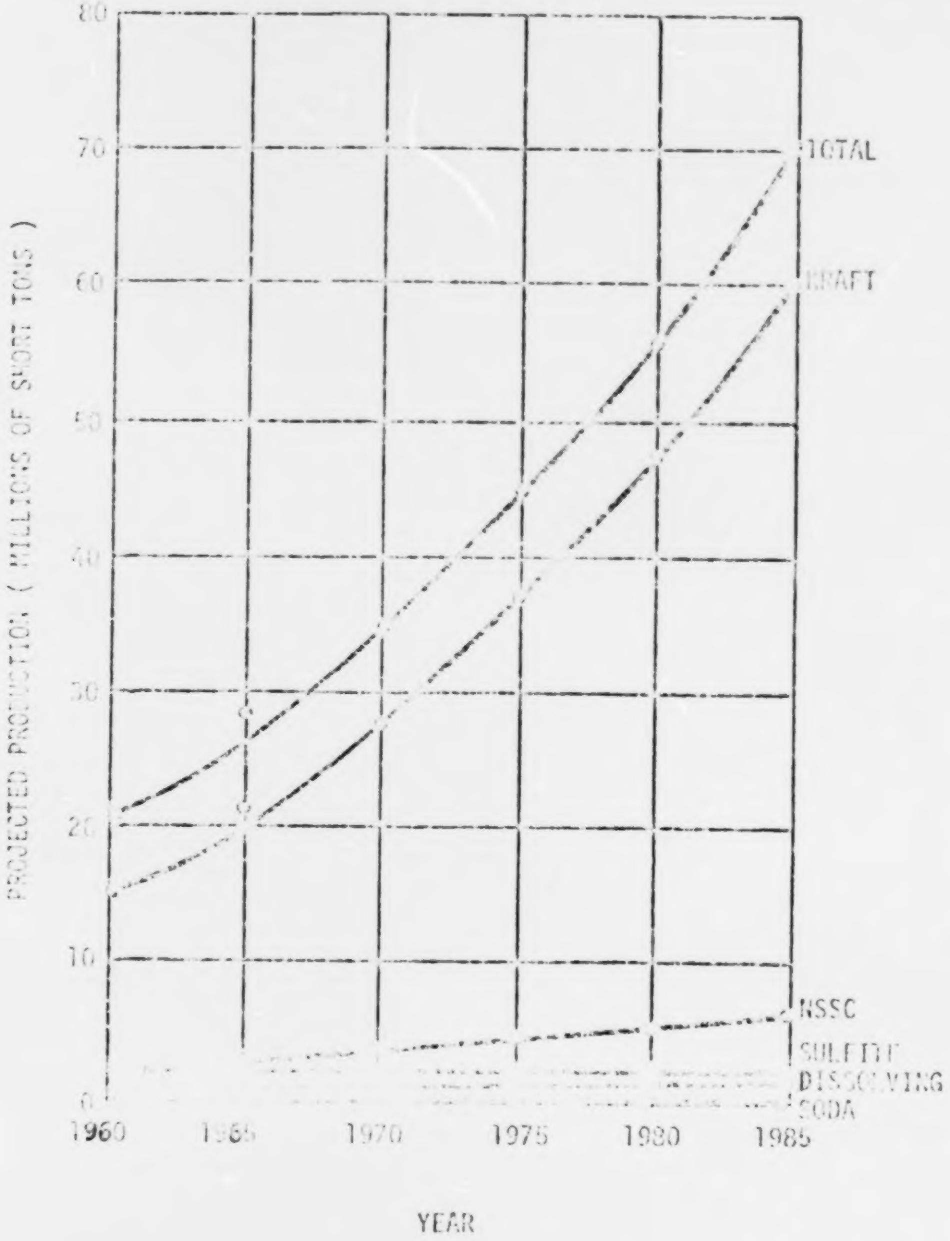

NSSC MILLS
SULFITE MILLS
REGION I
REGION II
REGION III
REGION IV
REGION V

REGIONAL DISTRIBUTION
OF SULFITE AND NSSC PULP MILLS
IN THE U. S.

FIGURE 2-2

FIGURE 2-3

PROJECTION OF PRODUCTION
OF CHEMICAL PULPS IN THE U. S.



Detailed breakdowns of Table 2-3 may be found in Appendix A (Tables A-4, A-5, A-6, and A-7).

TABLE 2-3

ANNOUNCED AND ESTIMATED EXPANSION AND PHASING OUT PLANS THROUGH 1980

I. Current and Planned New Plant Construction as of December 31, 1971[b]

	CAPACITY ADT/DAY		
	Kraft	Sulfite	NSSC
New	5,866 (12)	830 (2)	750 (3)
Expansion	2,135 (5)	0	568 (2)
TOTAL	8,001 (17)	830 (2)	1,318 (5)

II. Estimate of Phased Out Operations

	CAPACITY ADT/DAY			
Time Period	Kraft	Sulfite	NSSC	Soda
In 1968		835 (5)		60 (1)
In 1969-70	205 (1)	503 (3)	235 (1)	
In 1970-80	85 (1)	1,562 (17)		140 (2)
TOTAL	209 (2)	2,900 (25)	235 (1)	200 (3)

(b) Figures in ( ) indicate number of mills

In addition to the current and planned new plant construction shown above, there are at least twelve proposed or tentative mills in the talking stage of development. These twelve mills would, if brought to production, supply in excess of an additional 3,000 tons per day of pulp.

CHAPTER 3

PROCESS DESCRIPTIONS

3.1 DEFINITIONS

The following definitions are provided for the benefit of those not intimately familiar with the chemical wood pulping industry. In some instances definitions are given because of special meanings which a term may have in this report.

Particles - Any material which exists as a solid in a gas steam at duct conditions and is collected in accordance with EPA sampling procedures.

Trace - A quantitative expression of emissions which is less than 0.01 pounds per ton of air dry unbleached pulp.

Standard Conditions - 29.92 inches of mercury and 70 degrees F.

Sulfidity - An expression of the percentage makeup of chemicals in kraft cooking liquor obtained by the formula

$$\frac{Na_2S}{Na_2S + NaOH} \times 100$$

where the sodium compounds are expressed as Na_2O.

Yield - The percentage of a specific weight of bone dry wood that is converted to bone dry pulp.

Weak Wash - A liquid stream in the kraft process which results from washing of the lime mud. It is used mainly for dissolving smelt.

Smelt - The molten chemicals from the kraft recovery furnace consisting mostly of sodium sulfide and sodium carbonate.

Oxidation Efficiency - The percentage of sodium sulfide in the kraft black liquor which is oxidized by air introduced into the liquor. The Na_2S is usually expressed in grams per liter of black liquor.

Roundwood - Logs as delivered to the mill with bark attached and cut to specified lengths (up to 10 feet).

Board - A heavy sheet made with single or multiple plies of pulp formed on a board machine such as a fourdrinier.

Linerboard - A laminated container board usually made of kraft pulp. It consists of a base sheet which is coarse strong pulp and a top liner sheet which is fine pulp. The top liner gives the container board a more finished exposed surface than the base sheet.

Top Liner - A sheet, usually produced from kraft pulp, which is added as a laminate to the base sheet to produce linerboard. The pulp may in some cases be bleached.

Base Stock - A sheet, usually produced from unbleached kraft pulp, formed into linerboard on a fourdrinier machine.

Corrugating Medium - A sheet, usually made from NSSC pulp, which is corrugated to form a cushioning layer when attached to a single sheet or between two boards. The corrugating sheet is usually 0.009 inches thick and traditionally is referred to as "9 point."

Bark Boiler - A combustion unit used to produce steam for process or electrical energy which is designed to burn mainly bark and wood residues.

Combination Boiler - A combustion unit used to produce a steam for process or electrical energy which is designed to burn bark and at least one other fuel.

Power Boiler - A combustion unit used to produce steam for process or electrical energy which is designed to burn oil, coal, or gas.

Recovery Boiler - A combustion unit used to produce steam for pulping and recovery operations, and to recover the chemicals from the spent cooking liquor.

3.2 THE KRAFT PROCESS

The kraft process produces a dark colored fiber. Therefore, the market for the unbleached pulp is usually limited to its use in board, wrapping, and bag papers. If kraft pulp is to be used in the manufacture of fine white papers, its fibers must be treated additionally in a bleach plant.

The presence of caustic soda in the cooking liquor permits the pulping of practically all wood species. The other active chemical, sodium sulfide, creates a chemical reaction during cooking that imparts the strength characteristics to kraft fibers, producing fibers that are stronger than those made from NSSC or sulfite processes.

Small amounts of sodium sulfide react with lignin and carbohydrates in the wood to form odorous compounds which may cause a reduction of air quality.

In the kraft pulping process, shown in Figure 3-1, the white liquor --a solution of sodium sulfide and sodium hydroxide in water--is utilized to dissolve the lignin from wood and render cellulose fibers usable for pulp manufacture. The white liquor is mixed with wood chips in a digester where the chips are cooked for about three hours with 110 psig steam. During the cooking period, the digester is

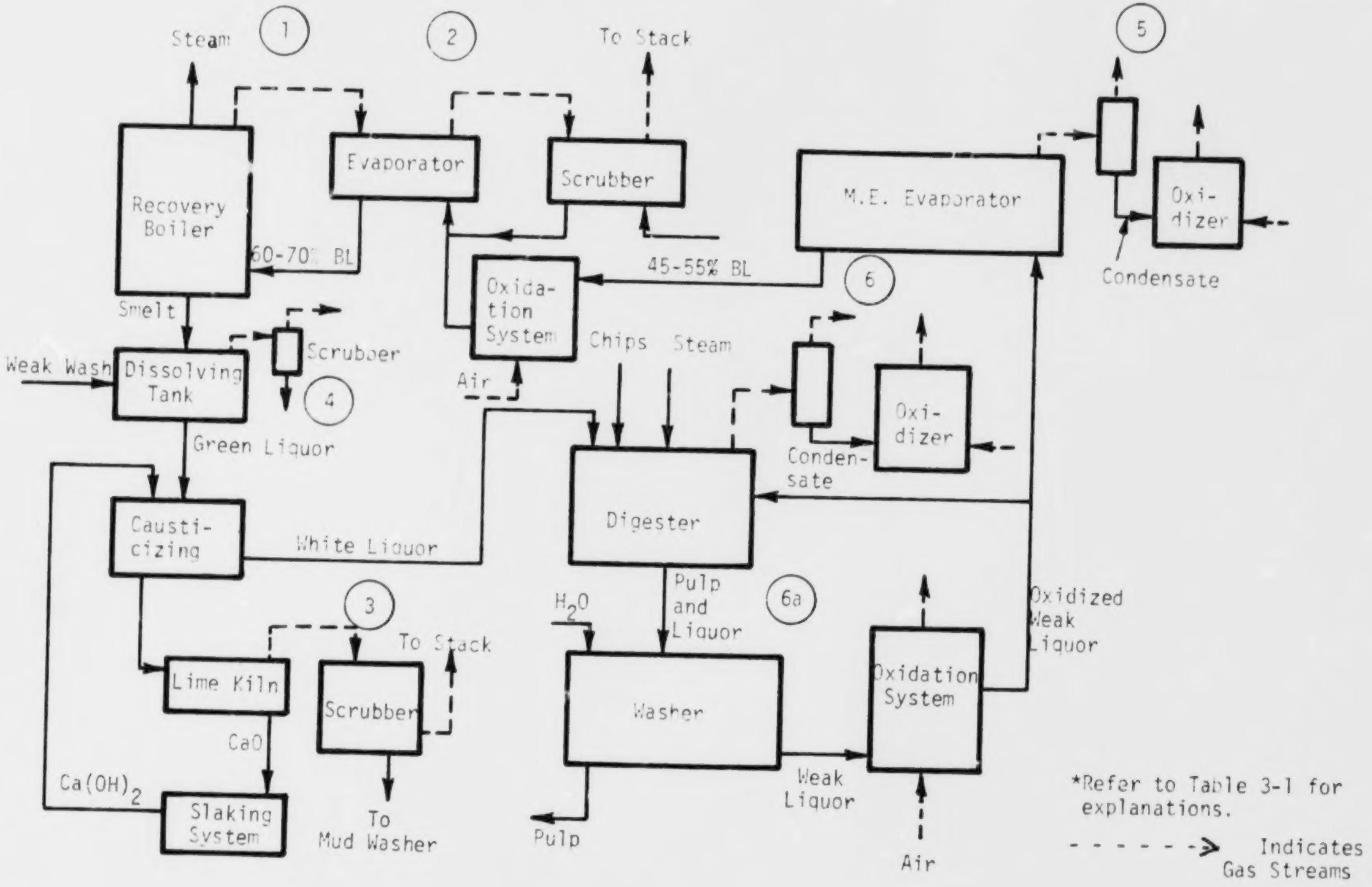

Steam
①
②
To Stack
⑤
Recovery Boiler
Evaporator
Scrubber
M.E. Evaporator
Oxi-dizer
60-70% BL
45-55% BL
Condensate
⑥
Smelt
Oxida-tion System
Chips
Steam
Weak Wash
Dissolving Tank
Scrubber
④
Air
Oxi-dizer
Green Liquor
Condensate
Digester
Causti-cizing
White Liquor
③
Pulp and Liquor
6a
H2O
Oxidized Weak Liquor
To Stack
Lime Kiln
Scrubber
Washer
Oxidation System
CaO
Ca(OH)2
Slaking System
To Mud Washer
Pulp
Weak Liquor
Air
*Refer to Table 3-1 for explanations.
- - - - - -> Indicates Gas Streams

FIGURE 3-1. KRAFT PULPING AND RECOVERY PROCESS

relieved periodically to reduce the pressure buildup of various gases generated within. When cooking is complete, the digester contents are forced into a blow tank where a major portion of the spent cooking liquor containing the dissolved lignin is drained. The pulp passes through the knotter, goes through various stages of washing and bleaching, and is then pressed and dried into the finished product.

The kraft recovery process essentially consists of the following major operations:

1. Concentration of weak black liquor from approximately 17 to 50 percent solids, in multiple effect evaporators.
2. Further concentration to 65 to 70 percent solids in an additional effect known as a concentrator or using the heat content of the recovery furnace flue gases in a direct contact evaporator.
3. The burning of the combustible concentrated black liquor in the recovery furnace to recover a portion of the heat by oxidation of the dissolved lignin and to recover the inorganic chemicals in the form of molten smelt.
4. The preparation of green liquor by dissolving the smelt (a mixture of sodium sulfide and sodium carbonate) with water and weak wash from the causticizing plant.
5. The preparation of white liquor in a causticizer where the sodium carbonate (from green liquor) is converted to sodium hydroxide by the addition of calcium hydroxide.
6. The conversion of the precipitated calcium carbonate to calcium hydroxide for reuse in the causticizer by burning the calcium carbonate in a lime kiln and then slaking the product calcium oxide.

In the kraft process, chemicals in the form of solids, mists, odorous and nonodorous gases may be emitted into the atmosphere, as summarized in Table 3.1. The recovery furnace potentially is the largest source of emission of solids and sulfur bearing gases. Digester relief gases, blow gases, and off gases from the evaporators represent a considerably smaller volume, but have a potentially higher nuisance value. Not only are these chemical losses costly, but they are air pollutants as well. The recovery furnace, multiple effect evaporator, lime kiln, and blow gases are the major source of heat loss.

In the following sections, the sources of emission, the theoretical explanation for the emissions, and the various processes and equipment used to reduce the chemicals and heat losses will be discussed in greater detail.

TABLE 3-1

SUMMARY OF MAJOR SOURCES AND TYPES OF CHEMICAL LOSSES

Source	Type of Chemical Loss Solids	 Odorous and Nonodorous Gases
1. Recovery Furnace	Sodium carbonate Sodium sulfate Carbon	Carbon monoxide Carbon dioxide Sulfur dioxide Hydrogen sulfide Methyl mercaptan Dimethyl sulfide Dimethyl disulfide
2. Direct contact evaporator	Same as recovery furnace	Same as digester
3. Lime kiln	Lime dust Soda dust	Sulfur dioxide Hydrogen sulfide
4. Dissolving tank	Sodium carbonate Sodium sulfate	Hydrogen sulfide
5. Multiple effect evaporator	None	Same as digester
6. Digester	None	Sulfur dioxide Hydrogen sulfide Methyl mercaptan Dimethyl sulfide Dimethyl disulfide
7. Blow Tank	None	Same as digester

TABLE 3-2

CHEMICAL EMISSIONS FROM THE RECOVERY FURNACE

Chemical	Emission	lb/ton of pulp	lb/day*
Sodium salts Na_2SO_4 Na_2CO_3	4.5 - 6.0 grains/ SCF dry	150 - 200	75,000 - 100,000
Hydrogen sulfide	900 - 1000 ppm	25 - 28	12,500 - 14,000
Methyl mercaptan	200 - 1000 ppm	8 - 40	4,000 - 20,000
Dimethyl sulfide	60 - 150 ppm	3 - 7.5	1,500 - 3,750
Sulfur dioxide	300 - 500 ppm	25 - 40	12,500 - 20,000

*For 500 tons/day pulp mill

3.2.1 DIGESTER AND BLOW TANK

During the cooking period, the digester is relieved periodically to reduce the pressure buildup of various gases within. These relief gases essentially contain steam, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. When cooking is completed, the digester contents are forced into the blow tank where a major portion of the spent cooking liquor containing dissolved lignin is drained. Gases similar in composition to the digester relief gases are released.

The formation of mercaptan and dimethyl sulfides in the digester result from reactions between sulfide and hydrosulfide ions and methoxyl group of lignin in the wood being pulped. During the digester relief when the pressure is suddenly released, mercaptan and sulfides will be carried off with the steam. Hydrogen sulfide will also be released due to a stripping reaction.

The quantity of dimethyl sulfide formed depends on the quantity of methyl mercaptide ion present. In long cooks at high temperature and sulfidity, the amount of dimethyl sulfide may exceed the methyl mercaptan. The quantity of mercaptan and sulfide formed is directly proportional to the digestion temperature and the sodium sulfide concentration in the cooking liquor. The quantity of mercaptan and sulfide is higher when pulping hardwoods than softwoods.

Various sulfur compounds of digester relief in lbs/ton of pulp include: Hydrogen sulfide, 0.01 to 0.05; Methyl mercaptan, 0.02 to 0.04; Dimethyl sulfide, 0.5 to 1.0; and Dimethyl disulfide, 0.1 to 0.5. Blow tank lbs/ton of pulp figures for the same gases are: Hydrogen sulfide, 0.1 to 0.5; Methyl mercaptan, 0.5 to 1.5; Dimethyl sulfide, 1.0 to 1.5; and Dimethyl disulfide, 0.5 to 2.0.

Various processes used in the industry to reduce and recover the sulfur loss and the odor include:

1. Oxidation of the noncondensible gases by burning in the recovery furnace, lime kiln, or other suitable devices.
2. Absorption by suitable alkaline solution such as white liquor using a venturi or packed tower type absorber.
3. Destruction of sulfur compounds by chlorination.

As the batch digester is relieved intermittently to avoid surging conditions, some mills collect the gases in a suitable container and then feed continuously to either a lime kiln or a recovery furnace. When a continuous digester is used, the surges are largely eliminated and no containment vessel is required. When burning these sulfur bearing gases at or above 1,400°F, complete combustion occurs of the organic sulfides and hydrogen sulfide to sulfur dioxide, carbon dioxide and water vapor. Since the firing end of the lime kiln operates at a temperature above

2,000°F, combustion of these gases in the lime kiln is most suitable. The sulfur dioxide generated will be efficiently absorbed in the venturi type lime kiln scrubber.

Chlorination, followed by caustic absorption, is a less effective means for treating the noncondensible sulfur compounds. Chlorine, being a powerful oxidizing agent, readily oxidizes organic sulfides and hydrogen sulfide to free sulfur, sulforyl or sulfoxy compounds. The gases leaving the chlorination stage are then absorbed in a caustic solution.

These methods of treatment effectively eliminate the odor caused by sulfur bearing gases. Where combustion is practiced, a suitable scrubber will efficiently recover the sulfur compounds formed as a result of combustion products.

Where wood with a turpentine content is cooked, there is a loss of turpentine whenever a digester is relieved. The resinous materials in certain pulpwoods, particularly the southern pines, give off turpentine vapor. The heat and turpentine are recovered simultaneously by condensing the digester relief gases in a condenser.

3.2.2 BROWN-STOCK WASHING

Two types of washing equipment used for removal of black liquor are the diffuser and the rotary-drum vacuum filter. In comparing the advantages of the vacuum washer and diffuser systems, some pulp mill operators consider that the time involved in the use of diffusers is a distinct advantage not present with vacuum washers in that the longer period of contact with wash water permits removal of soda from the pulp by leaching or diffusion.

The rotary-drum vacuum filter arranged for multistage countercurrent washing has become standard equipment in most of the pulp mills in the United States and Canada. Diffusers were generally used until about 1935; previously, vacuum washers had been considered unsatisfactory for washing pulp from resinous woods because of the serious foaming conditions which resulted. Foaming trouble was overcome by improvement in filter design, which prevented air from becoming entrained with the liquor.

For some time there have been no installations of diffusers, adoption of the rotary washer being general. Two, three, or four washers are used in series for multistage countercurrent washing, which reduces the amount of wash water required for the desired pulp cleanliness. The rotary vacuum filter with multiple port valves has been designed for two and even more stages of washing on the same drum. These systems are more complex and require close and accurate control owing to the splitting of the filtrate and the time element required for the liquor to pass through the sheet and reach the valve. These washers have met with success where the throughput is maintained within an extremely limited range.

3.2.2.1 The Washing Operation

A typical brown-stock operation is made up of a series of rotary-drum vacuum filters with intermediate repulpers for redilution and agitation of the pulp sheet. Almost all the systems in the United States use a single liquor displacement on each washer. Although the washing system and its operation may be complex, the fundamentals are as simple as those of the age-old washing of clothes. When a limited amount of water is available, washing is best accomplished by scrubbing the clothes in part of the water, wringing thoroughly, and repeating several times. In pulp washing, this is the essential process, except that it is on a continuous basis, with a small amount of water added in the final stage and a like amount flowing countercurrent to the middle stage, or stages, and then to the first stage. The liquid entering the system with the blow and the amount of water entering at the last stage minus the water in the sheet then carry the soluble solids out of the first stage to the evaporating system, and the washed pulp is discharged from the final washer.

The vacuum filter is excellent for this soluble solids reduction because it allows the liquid entering each stage to be displaced through the thin mat of stock as it travels over the exposed area of the filter. A uniform application of wash liquor will achieve a higher degree of displacement of the vat liquor in the sheet and result in a higher displacement ratio. Although the displacement of wash liquid in the sheet is important, essential work is done in the intermediate repulpers between the stages where the thickened sheet of pulp is diluted and scrubbed with the weaker liquor of the subsequent stage. Here fibers are agitated in as low a consistency of slurry as possible in order to achieve the minimum concentration of dissolved solids prior to the extraction on the following vacuum filter. Low vat consistency promotes diffusion of the strong liquor at the fiber wall.

Emissions from brown stock washers consist of H_2S and TRS ranging from 0.01 to 0.08 and 0.12 to 0.45 lbs/air dry ton respectively. Control methods consists of those alternatives employed for other relief and non-condensable gases.

3.2.3 BLEACH PLANT

Bleaching of chemical pulps is, in a sense, the continuation of digestion. The placement of the dividing line is sometimes a matter of relative costs. Thus, a pulp mill with high wood costs but cheap power and chemicals (some of which may be of mill manufacture) may decide-- within limits-- to end the cooks while the pulp retains a relatively high portion of lignin and to complete the delignification with the more selective bleaching chemicals as a means of achieving higher yield. A pulp mill with low wood costs and expensive bleaching chemicals will sacrifice some pulp yield and cook to the lowest Kappa number which still gives the desired pulp qualities. Whatever the situation, digestion must be properly and uniformly conducted, and in most cases the aim is to remove in cooking as much of the lignin as feasible.

Our commercial cooking processes, most of which proceed in a reducing system at rather high temperature, cannot be pushed to complete delignification without serious damage to the fibers. All the lignin can, however, be eliminated by some oxidizers (as for instance chlorine dioxide), but reaction time is long and costs are high and even in this case there is always the danger of carbohydrate degradation. Thus, the production of white wood fibers depends on a combination of cooking and bleaching.

3.2.3.1 Basic Principles

The discovery of chlorine by Scheele in 1774 and the subsequent preparation of calcium hypochlorite by Tennant initiated the use of chemicals in the bleaching of cellulose fibers. Initially, equipment and process were rather crude, and it was only about 150 years later that a measure of control was established and reproducible results were obtained. During all this time the mills endeavored to do on chemical pulps with one bleaching agent (calcium hypochlorite) a job which, as we know today, cannot be done efficiently ine one operation. There is at present no single chemical substance which answers all the requirements of a commercial pulp-bleaching agent, so that it is necessary to resort to a number of chemicals, which in turn recommends the division of the process into a series of separate treatments. Experience gained and studies made since about 1925 furnish a good foundation for the chemical bleaching of cellulose, and although many details are still obscure, enough knowledge has been developed to build bleach plants which yield the desired product.

A bleaching stage normally consists of equipment to bring the stock to the desired consistency, a mixer that will blend chemical, fibers, and steam, a retention vessel wherein the reaction may proceed, and a washer for the separation of the treated fibers from the waste products. A series of such stages is called a bleaching sequence.

Unfortunately, none of the chemicals at our disposal is absolutely specific, which means that in every case there is some unwanted action upon the pulp fibers. It is, therefore, necessary to find out how much of the respective agent can be efficiently applied, and experience has confirmed the expectation that smaller amounts are better than larger ones. On that basis, one would conclude that the more stages used the better the results. This is quite true, as long as each stage provides sufficient reaction time for the lenient conditions then existing. However, it will be found that capital, maintenance costs, and operating costs put a low ceiling on the number of stages, and a compromise must be made between academic goals and practicality.

Elemental chlorine is universally used for lignin fragmentation. It measures up well to the above requirements. Its specificity for lignin is excellent, and the reaction proceeds so fast and completely that any attack upon the carbohydrates can be prevented. Chlorine dioxide is also suitable in some respects--and is perhaps even superior--so that it may be used in substitution if its present cost differential with chlorine can be reduced.

The products of pulp chlorination and of the oxidative bleaching stages are more soluble in an alkaline medium than in water, and they are generally taken out of the system by an alkaline extraction. For good efficiency, temperature and pH of these extractions must be high, the latter at least above 10 and frequently above 11. Such high values are not, however, compatible with those of the bleaching reactions, so that separate extraction stages are recommended for all bleaching agents except peroxides. In many cases these extraction stages also serve the removal of resin and hemicelluloses. Caustic soda is the preferred agent, but other alkalis have been used.

3.2.4 MULTIPLE EFFECT EVAPORATORS

In a multiple effect evaporator, black liquor is concentrated from 16% solids to about 50 to 55% solids in several successive stages. The dilute black liquor that enters the evaporator contains some methyl mercaptan dissolved in the alkaline solution. Douglass and co-workers (16) reported that about 0.38 pounds of methyl mercaptan per ton of pulp production and only a negligible quantity of dimethyl sulfide enter the evaporator. The concentrated black liquor contains less residual mercaptan than the amount that entered with weak liquor.

This means most of the original mercaptan is stripped off during evaporation. During the final evaporation stage, there is appreciable formation of methyl mercaptan. This may be a result of the high concentration of chemical reactants and the high temperature that exists in the final evaporation stage. A small quantity of dimethyl sulfide is also formed. Douglass (16) concluded that most of the mercaptan found in the vapor and condensate from the multiple effect evaporator is the same as that present in the black liquor entering the evaporator.

Hydrogen sulfide and methyl mercaptan are the major constituents found in the noncondensible gases and the condensate leaving the evaporators. The hydrogen sulfide emission may vary between 1 to 3 lbs/ton of pulp , whereas the mercaptan emission may be as high as 0.5 lbs/ton of pulp. The condensate also carries the same odorous compounds.

3.2.4.1 Effect of Oxidation

Weak black liquor oxidation has been found effective in significantly reducing the release of odorous compounds. Almost 90% reduction can be attained with essentially 100% oxidation efficiency. In recent findings, Shah and Stephenson (8) reported that condensate from the multiple effect evaporators, including both the condensate from the liquor vapors and the jet condensers, had very little noticeable odor. The biochemical oxygen demand was reduced by almost 28% and the pH was alkaline. As a result, the condensate is suitable for reuse in the process as hot water.

Chlorination is another means for treating the noncondensible sulfur compounds. In some cases, the waste hypochlorite bleach liquor is used to treat these gases. Dimethyl sulfide is oxidized in the presence of chlorine to a water soluble and essentially odorless compound dimethyl sulfoxide.

The complex reactions between methyl mercaptan and chlorine result in high boiling, hence, less volatile compounds. In most cases, the chlorination stage is followed by caustic absorption. Packed and plate towers and low pressure drop venturi type absorbers are widely used as chlorine caustic scrubbers. This treatment results in essentially complete absorption of sulfur compounds, but the sulfur recovered will be a loss for the pulping process as the resulting solution will be discharged to the sewer.

In some cases, the malodorous gases are collected and then burned in either a lime kiln or other suitable furnace. This is a more economical and more effective means of disposal and/or recovery than by chlorination. The chemical reaction are:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$2CH_3SCH_2 + 9O_2 \rightarrow 4CO_2 + 2SO_2 + 6H_2O$$

$$CH_3SH + 3O_2 \rightarrow CO_2 + SO_2 + 2H_2O$$

This method of recovery has limited application potential due to certain explosion dangers. For safe handling, it is recommented these gases be diluted with large volumes of air. In case these gases are burned in the lime kiln, the sulfur dioxide produced will be efficiently absorbed in a venturi type lime kiln scrubber. It these gases are burned in a separator reactor, a caustic or carbonate scrubber will be most effective for sulfur dioxide recovery.

3.2.5 BLACK LIQUOR OXIDATION (BLO)

The release of malodorous gases, such as hydrogen sulfide, mercaptan's, methyl sulfides and disulfides, and sulfur dioxide can be reduced significantly if the black liquor is oxidized. In recent years, black liquor oxidation has become an integral part of the kraft recovery process because of its high potential for reducing odor and sulfur losses from conventional boilers. Black liquor is oxidized either prior to the recovery boiler or multiple effect evaporation, depending on the specific application.

The development of various oxidation systems is a direct result of continuing research to reduce the emission of odorous gases which contribute to the typical characteristic odor associated with kraft pulping. The black liquor oxidation (BLO) not only reduces odor and chemical losses from the recovery furnace and the direct contact evaporator, but also reduces the chemical losses from multiple effect evaporators if weak black liquor is oxidized.

In the kraft pulping industry, both weak and strong black liquor oxidation are practiced. The oxidation of weak black liquor offers more benefits such as lower operating costs, reduction in sulfur loss from multiple effect evaporators, increased soap yield, etc. than strong black liquor oxidation. The weak black liquor is the liquor at 12 to

18% solids concentration entering the multiple effect evaporators, whereas the strong liquor is 45 to 55% solids concentration leaving the multiple effect evaporators.

The strong black liquor oxidation is practiced greatly in the southern U.S. mills using southern pine as wood furnish. The weak black liquor resulting from the pine resinous woods has the tendency to foam excessively. The soap content of the black liquor essentailly determines the extent of the foam formation. The foam has been found to be very difficult to handle. Recently, a successful operation of the commercial weak black liquor oxidation plant handling 60% pine wood furnish has been reported.

The oxidation of black liquor and its advantages have been described in detail. Figures 3-8 and 3-9 show typical weak and strong black liquor systems showing the various equipments, i.e. oxidation tower, foam tank, foam breakers and cyclones. The arrangement of the equipment may vary from one supplier to another. The oxidation tower may be a plate tower, packed tower or other suitable type, and the liquor and air flows may be cocurrent or countercurrent.

Black liquor oxidation application to southern pine liquors has mainly been restricted to the compressed air sparger - retention tank system because of the inherent foam problem. Recently, there have been a few successful attempts at oxidizing southern kraft weak black liquor in conventional mass transfer systems.

In the black liquor oxidation, the liquor and oxidizing agent, such as air, are brought into intimate contact. The oxidized liquor, air, and foam then enter the foam tank where oxidized liquor is separated from air and foam. The air and foam then enter the foam breakers where foam is converted to liquor which is returned to oxidized liquor storage tanks. The clean air is discharged into the atmosphere after separation of entrained liquor in a cyclone. The objective of BLO is to produce a liquor in which the sulfides are less than 0.1 gram per liter.

The chemical reactions involved in black liquor oxidation are complex since the organic material as well as the sulfur bearing compounds react with the oxygen content of the air. The overall oxidation reactions are:

$$\begin{aligned} &2Na_2S + 2O_2 + H_2O \\ &\rightarrow Na_2S_2O_3 + 2NaOH \end{aligned}$$

$$\begin{aligned} &4CH_3S\,Na + O_2 + 2H_2O \\ &\rightarrow 2CH_3S\,SCH_3 + 4NaOH \end{aligned}$$

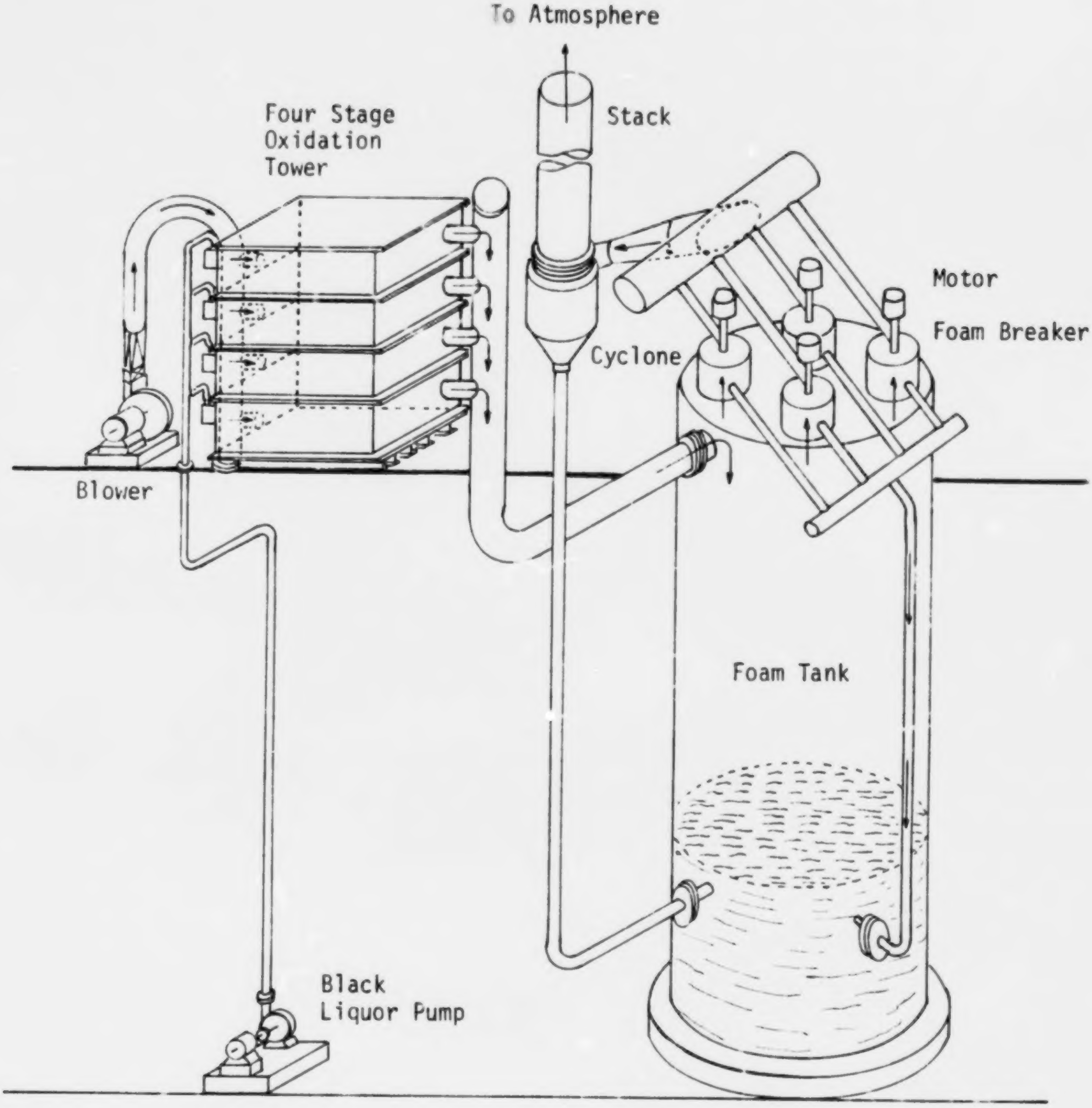

To Atmosphere
Four Stage Oxidation Tower
Stack
Motor
Foam Breaker
Cyclone
Blower
Foam Tank
Black Liquor Pump

FIGURE 3-8 THE SCHEMATIC ARRANGEMENT OF THE COMMERCIAL OXIDATION SYSTEM

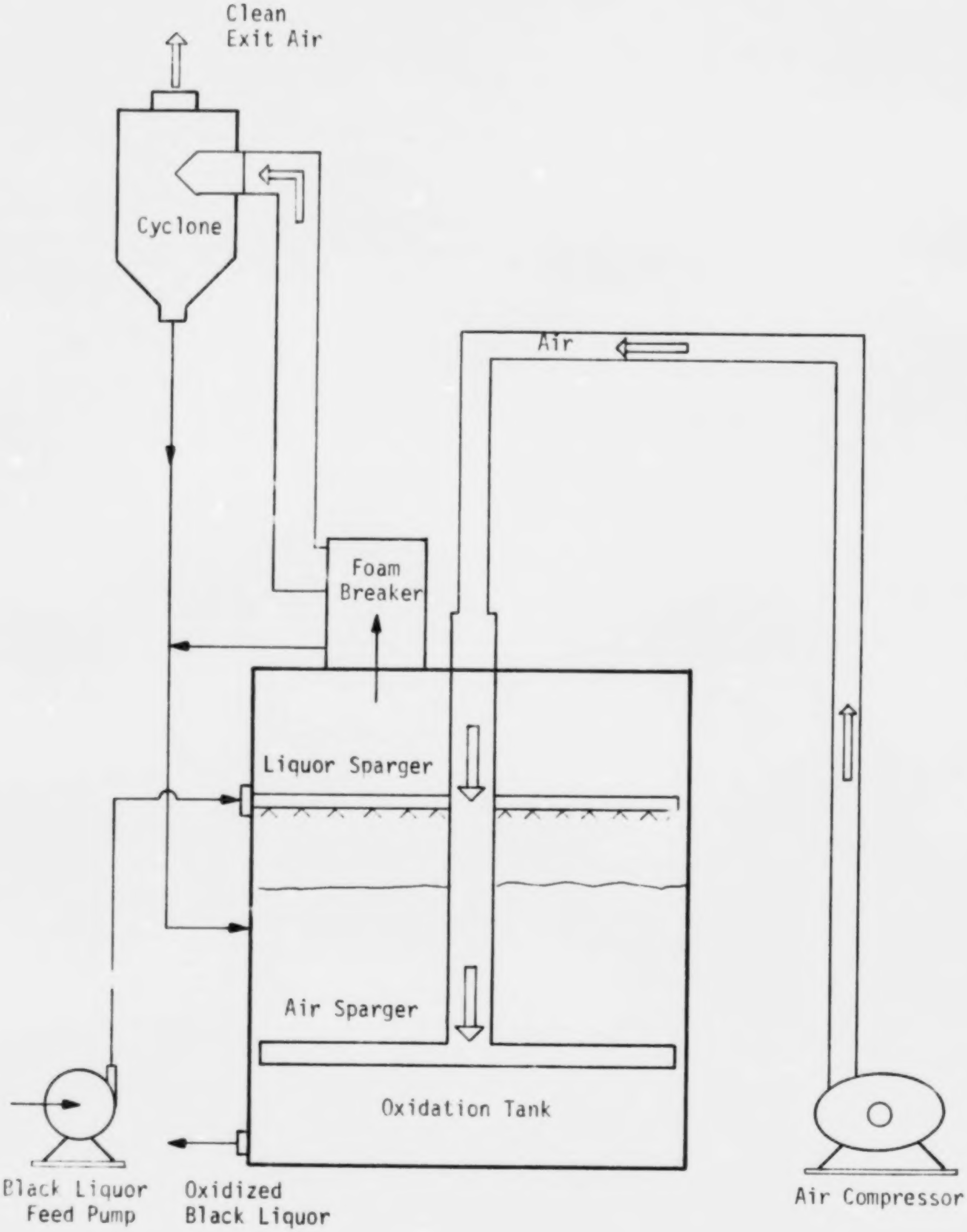

Clean
Exit Air
Cyclone
Air
Foam
Breaker
Liquor Sparger
Air Sparger
Oxidation Tank
Black Liquor
Feed Pump
Oxidized
Black Liquor
Air Compressor

FIGURE 3-9 OXIDATION SYSTEM FOR STRONG BLACK LIQUOR CHAMPION PROCESS

In the case when black liquor is oxidized at too low a temperature, elemental sulfur instead of thiosulfate will be formed. This should be avoided because during evaporation of the liquor, the elemental sulfur reacts with hydroxide at higher temperatures, reverting partially to sulfide ions.

3.2.5.1 Effect of BLO

The value of black liquor oxidation for a kraft mill operating under the overload conditions of a recovery furnace really depends upon the operation of the direct contact evaporator or scrubber installed for recovering the heat and chemicals from the flue gases. Black liquor oxidation cannot control hydrogen sulfide emission from the recovery furnace under the overload conditions, as the hydrogen sulfide emission is primarily affected by the ratio of air to black liquor solids at the furnace hearth and the method of air distribution.

To reduce the concentration of hydrogen sulfide in the flue gases leaving the stack, the direct contact evaporator or scrubber play a very prominant role. The oxidized black liquor contains sodium thiosulfate and essentailly no sodium sulfide. The carbon dioxide and sulfur dioxide gases do not react with sodium thiosulfate. Thus, hydrogen sulfide generation does not take place. Also, the sodium hydroxide formed during oxidation reacts with sulfur dioxide and hydrogen sulfide in the flue gas and thus increases the absorption of both gases. This clearly indicates that oxidation of black liquor reduces the concentration of sulfur dioxide and hydrogen sulfide in the flue gases leaving the stack of conventional boilers.

The following explains what happens in the recovery furnace when oxidized liquor is fired.

The sodium thiosulfate will decompose in the furnace to sodium sulfite and sulfur. In an oxidizing atmosphere, the elemental sulfur is converted to sulfur dioxide which reacts with sodium carbonate to form sodium sulfite and is further oxidized to sodium sulfate.

The overall reactions are as follows:

$$Na_2S_2O_3 \rightarrow Na_2SO_3 + S$$

$$S + O_2 \rightarrow SO_2$$

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4$$

The amount of sulfur dioxide emission from the recovery furnace is proportional to the concentration of sodium thiosulfate in the black liquor. Theoretically, for every mole of sodium sulfide oxidized, ½ mole of sulfur dioxide should be emitted. However, due to high availability of sodium carbonate in the recovery furnace, the actual emission is less. It is observed that for a mill practicing oxidation, the sulfur dioxide concentration in the flue gases leaving the recovery furnace increases. But in the case of mills using the venturi type evaporator and scrubber, this sulfur dioxide will be efficiently absorbed. If the reducing atmosphere exists in the recovery furnace, then the elemental sulfur will be converted to hydrogen sulfide instead of sulfur dioxide.

With the oxidation of black liquor, the hydrogen sulfide concentration leaving the recovery furnace stack can be reduced by 90 to 98%, and a significant reduction of odor can be attained. With black liquor oxidation efficiency essentially 100%, and by proper operation of the recovery furnace, it is possible: to reduce concentrations of hydrogen sulfide to 1 to 2 ppm; methyl mercaptan to 1 to 3 ppm; and dimethyl sulfide to 1 to 2 ppm. Even with these low concentrations, the typical kraft mill odor can still be detected since these compounds can be sensed down to the range of a few parts per billion.

3.2.6 THE RECOVERY FURNACE

Potentially, the major source of chemical and heat loss in the kraft pulping process is the recovery furnace which is the heart of the recovery process. Since the inception of the kraft recovery process, significant progress has been made in reducing the loss of heat and chemicals from the recovery furnace.

The flue gases leaving the recovery furnace contain not only 90 to 200 pounds of sodium compounds (mainly sodium sulfate and sodium carbonate) per ton of pulp production, but also 35 to 50 pounds of sulfur bearing malodorous gases such as hydrogen sulfide, sulfur dioxide, methyl mercaptan, dimethyl sulfides, and disulfides.

In the recovery furnace, heat is obtained from the combustion of the organic constituents of the black liquor, and the inorganic constituents are recovered as a molten smelt. The concentrated black liquor at 65 to 70 percent solids content is sprayed into the furnace where the water content is flashed off. As a result of pyrolysis, tne organic matter forms volatile products which burn in presence of oxygen. The combustion products, sulfur dioxide and carbon dioxide, react with sodium compounds to form sodium sulfite and sodium carbonate. The hot carbon from the pyrolized organic matter reduces the sulfur sodium compounds to sodium sulfide. The smelt that leaves the furnace essentially contains sodium sulfide and sodium carbonate.

While the black liquor is burned in the furnace, an appreciable quantity of sodium compounds are sublimed. As the combustion gases cool, the sublimate condenses and is entrained in the gas stream as a very finely dispersed fume (essentially sodium sulfate and sodium carbonate). Most of this is reclaimed by deposition on the heating surfaces of the recovery furnace and on the wetted surfaces of the direct contact evaporator if one is used. The remainder, in suspension in the flue gas as very fine solid particles, passes from the unit. The quantity of sodium (largely as sodium sulfate) in the flue gas, depends upon service conditions and operating care of the recovery furnace. It will vary from 90 to 200 pounds with an average of about 150 lbs/ton of pulp. For a 1000 ton/day pulp production, this abounts to 75 tons/day of dust entrained in the flue gases. This chemical loss in not only costly, but it is also a nuisance as an air pollutant.

The sulfur bearing malodorous gases, such as hydrogen sulfide, sulfur dioxide, methyl mercaptan, dimethyl sulfides and disulfides, represent another source of chemical loss and air pollution. Large volumes of hydrogen sulfide may be formed in the recovery furnace and, unless optimum combustion conditions exist, it will be discharged to the atmosphere.

The hydrogen sulfide emissions from a kraft recovery furnace is primarily affected by the ratio of air to black liquor solids at the furnace hearth and the method of air distribution. If a proper balance is maintained between the black liquor feed and the air input, a complete combustion of all pyrolysis products can be attained and all reduced sulfur gases will be converted to sulfur dioxide. The theoretical air requirements for complete combustion of a typical kraft black liquor and production of smelt of the desired composition are of the order of four to six pounds of air per pound of black liquor solids. As the kraft recovery furnace is overloaded, the amount of air and its distribution become limited by the forced draft and induced draft fan capacities. The forced draft fan "pushes" the combustion air into the furance, and the induced draft fan "pulls" the combustion from the furnace. Consequently, reducing conditions in the hearth or char bed become more pronounced, thereby generating increased quantities of hydrogen sulfide. This increased hydrogen sulfide generation is a function primarily of gas composition in equilibrium with the liquid solid phase at the furnace hearth. The air to solids ratio has a very promounced effect on the concentration of hydrogen sulfide and sulfur dioxide in the flue gases leaving the recovery furnace.

In present day practice, the recovery furnace functions as both a chemical reactor and steam generator--the steam generation function tends to predominate with older mills. The recovery furnace can be overloaded to achieve increased pulp productions and increased steam requirements. Increased pulp productions mean increase in the firing rate of black liquor. As the amount of black liquor solids fired increases, the ratio of air to solids decreases, which results in the increased generation of hydrogen sulfide. To obtain increased quantity of steam, the flue gas temperature entering the superheater section of the furnace has to be maintained at maximum. This can be attained by using the minimum quantity of air practicable or by using auxiliary fuel. This results in a decrease in the ratio of air to solids and hence an increase in generation of hydrogen sulfide.

Table 3-2 summarizes the type and quantity of chemical losses occurring at the recovery furnace. The gaseous emissions are based on the assumption that the mill does not practice any black liquor oxidation. The quantities may vary from mill to mill. It can be seen that the chemical losses from the recovery furnace can vary from 53 to 80 tons per day.

3.2.7 DIRECT CONTACT EVAPORATOR

In the classic kraft process, flue gases leaving the recovery furnace pass through the direct contact evaporator (DCE), where as a result of heat and mass transfer, the concentrated liquor from multiple effect evaporators is further concentrated to 65 to 70 percent. Some mills built since about 1968 do not utilize direct contact evaporators, but provide the additional concentration by an additional stage of multiple effect. In general, four types of direct contact evaporators are used: the cascade, the cyclone, the P-A venturi, and the two-stage venturi scrubber. In all four evaporators, the sensible heat content of the flue gas leaving the recovery furnace is utilized to further concentrate the black liquor from multiple effect evaporators prior to firing in the recovery furnace. The carbon dioxide (16 to 17 percent by volume) and sulfur dioxide (300 to 500 ppm) present in the flue gas react with the sodium sulfide content of black liquor and release hydrogen sulfide according to the following reactions:

$$\begin{array}{l} Na_2S + CO_2 + H_2O \\ \rightarrow Na_2CO_3 + H_2S \end{array}$$

$$\begin{array}{l} Na_2S + SO_2 + H_2O \\ \rightarrow Na_2SO_3 + H_2S \end{array}$$

Depending upon the sulfide ion concentration and the pH of the black liquor and the mixture of gases in the incoming gas stream, the direct contact evaporator may either emit hydrogen sulfide or absorb sulfur dioxide and hydrogen sulfide. Some of the sulfur dioxide in the furnace flue gas is absorbed by reacting with sodium carbonate, thus forming sodium sulfite:

$$\begin{array}{l} Na_2CO_3 + SO_2 \\ \rightarrow Na_2SO_3 + CO_2 \end{array}$$

The extent to which sulfur dioxide is absorbed largely depends upon the type of direct contact evaporator that follows the recovery furnace. The venturi type evaporators provide the best absorption efficiency as compared to the cascade and cyclone types.

3.2.8 RECOVERY FURNACE SYSTEM

In recovery furnaces which utilize any type of DCE, it is very difficult to distinguish the emissions evolved from the furnace alone as opposed to the combined emissions exiting the DCE and into the stack. In a case such as this, the equipment combination may be referred to as the recovery furnace system.

3.2.8.1 Control of Particulate Emissions From the Conventional Recovery Furnace System

For the recovery of chemicals in particulate form (sodium sulfate and other salts) from the flue gas leaving the recovery furnace, there are four systems offered to the kraft pulping industry:

1. The two-stage evaporator-scrubber system.
2. The cascade-precipitator system.
3. The cyclone-precipitator system.
4. The P-A (Pease-Anthony) venturi evaporator-scrubber system.

The cascade-precipitator and cyclone-precipitator systems are very similar in performance and operation.

The two-stage evaporator-scrubber system shown in Figure 3-2 consists of a venturi evaporator and venturi scrubber. The flue gas from the recovery furnace enters the venturi evaporator and contacts the liquor to be concentrated. As a result of simultaneous heat and mass transfer, the liquor is concentrated to the desired solids concentration for firing in the recovery furnace. The make up liquor to evaporator is either liquor from the multiple effect evaporator or a mixture of such liquor and bleed from the second stage scrubber, depending on what liquor is being used in the second stage as a scrubbing medium. The gas then enters the venturi scrubber where all the energy (pressure drop) is essentially utilized for scrubbing and optimum dust collection efficiency is attained.

The cascade-precipitator system shown in Figure 3-3 consists of a cascade evaporator and an electrostatic precipitator. Further concentration of black liquor from a multiple effect evaporator is accomplished in a cascade evaporator using the recovery furnace flue gases. The modern cascade evaporator consists of from one to four wheels in parallel and/or series configurations. The arrangement and amount of heating surface required depend upon the weight and temperature of gas and the desired final concentration of black liquor. The gas temperature leaving the cascade and cyclone evaporators is normally maintained at 300°F or higher. If the gas temperature entering the precipator is less than 300°F, local cold spots develop and result in condensation, fouling and rapid corrosion of the precipitator.

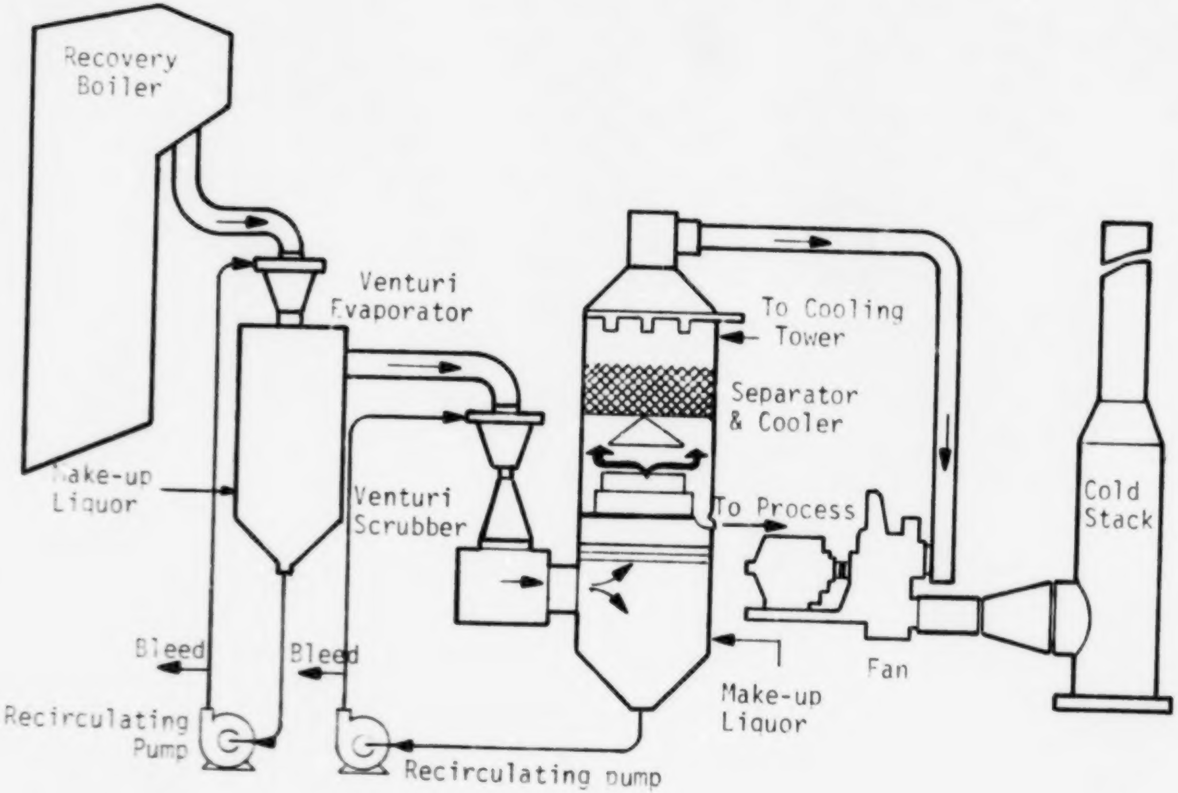

Recovery
Boiler
Make-up
Liquor
Venturi
Evaporator
Bleed
Recirculating
Pump
Venturi
Scrubber
Bleed
Recirculating pump
To Cooling
Tower
Separator
& Cooler
To Process
Make-up
Liquor
Fan
Cold
Stack

FIGURE 3-2. TWO STAGE VENTURI EVAPORATION - SCRUBBING SYSTEM

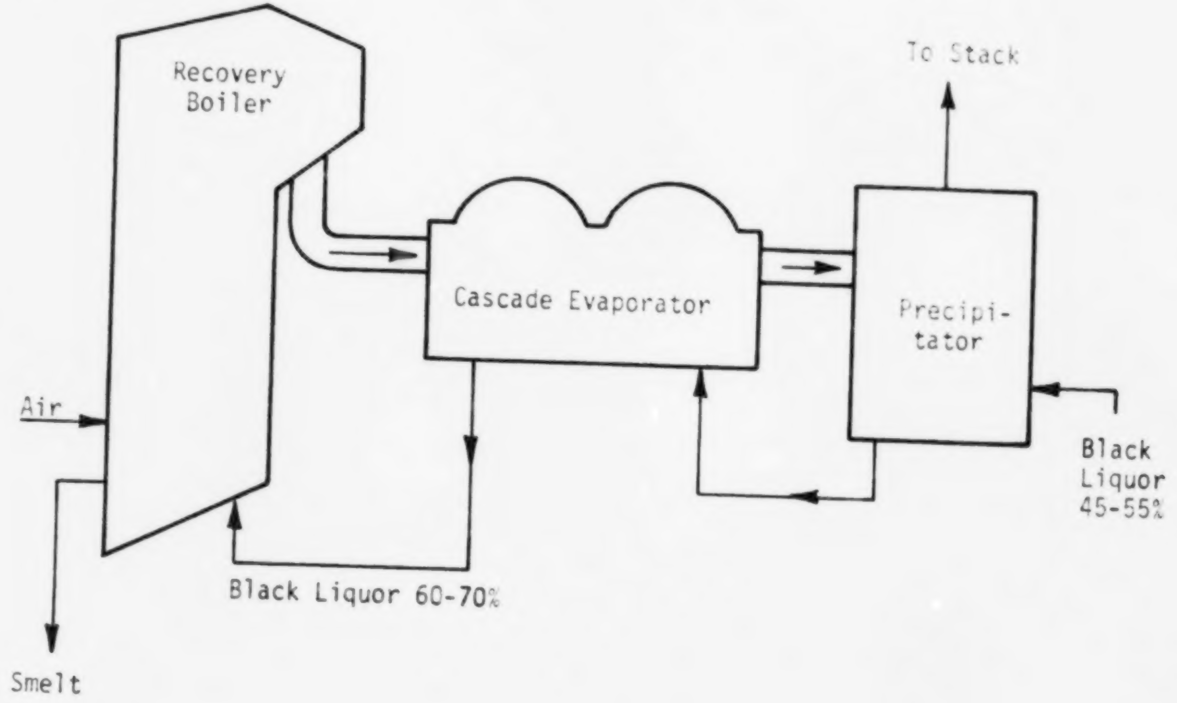

Recovery Boiler
Cascade Evaporator
Precipi-tator
To Stack
Black Liquor 45-55%
Black Liquor 60-70%
Air
Smelt

FIGURE 3-3. CASCADE PRECIPITATOR SYSTEM

The flue gas leaving the contact evaporator then enters the electrostatic precipitator where the sodium compounds--in dust form--are collected. The precipitator is operated on the principle that a particle suspended in the flue gas, if subjected to a sufficiently strong electrostatic field, becomes charged electrically and tends to migrate toward and adhere to an oppositely charged electrode. The collection electrodes are mechanically rapped periodically to shake the particles loose into a hopper or a vat of liquor. To energize the precipitator, potentials of 75,000 to 100,000 volts are necessary. The important factors for efficient precipitator operation are the gas temperature, moisture content, velocity and the retention time within the area subject to electrical charge.

In the P-A venturi evaporator-scrubber system shown in Figure 3-4, both the collection of dust from the flue gas and concentration of liquor by evaporation are accomplished simultaneously in a venturi type device. The system's operating principle is the collision of dust particles with liquid droplets formed by atomization and high velocity gas impact with liquor. The liquid droplets, with their dust particles entrapped, are then separated from the flue gas in a cyclonic separator.

The operating and performance characteristics of the three systems are summarized in Table 3-3. With the use of a two-stage evaporator-scrubber system, the chemical loss in the form of dust can be reduced by more than 90%. The total particulate matter loss can be reduced to 750 to 1,000 lbs/day for a 500 tons/day pulp production. Similar performance can be obtained by combining a cascade evaporator or cyclone evaporator with secondary scrubbing.

The secondary scrubbing systems shown in Figures 3-5 and 3-6, namely cyclonic and venturi, offer a solution to upgrade the dust collection and/or thermal efficiencies of the existing cascade-or cyclone-precipitator system. Table 4 summarizes the operating performance of the secondary scrubbing systems. The cyclonic scrubber system eliminates precipitator snow out problems and provides efficient heat and chemical recovery. This system's performance is excellent as a backup scrubber after an efficient precipitator. When the precipitator is down for major overhaul or for replacement, and when its performance has deterorated, a cyclonic scrubber alone cannot provide adequate dust collection efficiency. However, if a venturi type scrubber system is used following the precipitator, and should it become necessary to take the precipitator off line for some period of time, the venturi scrubber with proper static energy applied may perform adequate emission control alone. Many mills do not have nor need a secondary scrubber on this source.

With a precipitator efficiency of only 80 percent, the (secondary) cyclonic scrubber can provide 90 percent efficiency on emissions leaving the precipitator, for a total of 88 percent efficiency, at a pressure drop of 4 to 6 inches W.G. Likewise, a (secondary) venturi scrubber system can

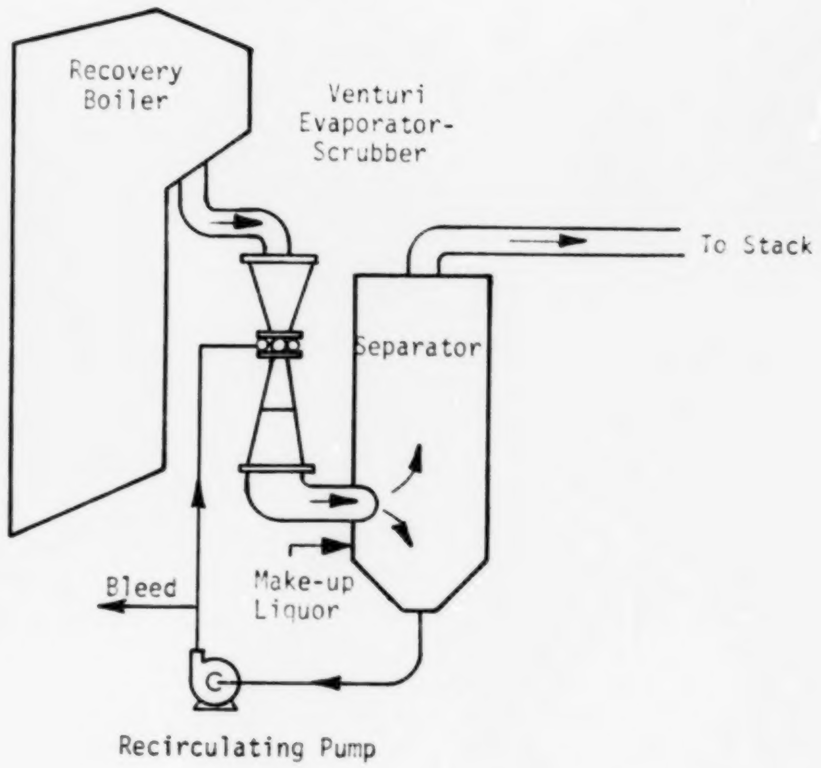

Recovery Boiler
Venturi Evaporator-Scrubber
To Stack
Separator
Bleed
Make-up Liquor
Recirculating Pump

FIGURE 3-4. VENTURI EVAPORATOR-SCRUBBER SYSTEM

TABLE 3-3

OPERATING AND PERFORMANCE CHARACTERISTICS OF SYSTEMS FOLLOWING RECOVERY FURNACE

	Two Stage Evaporator Scrubber System	Cascade Precipitator System	P-A Venturi Scrubber System
Gas temperature			
°F In	600	600	600
°F Out	150	300	190
Liquor concentration			
% Solids In	Evap-45 Scrub-17	45 - 50	45 - 50
% Solids Out	60 - 70 -30	60 - 70	60 - 65
Dust loading GR/SCF dry			
In	4.0	4.0	4.0
Out	0.04	0.08 - 0.4	0.4 - 0.8
Na_2SO_4 lb/ton of pulp			
In	150	150	150
Out	1.5	3 - 15	15 - 30
Efficiency %	99.0+	90 - 98	80 - 90
Pressure drop "WG"	30 - 35	8 - 10	35 - 40
Snow Out problem	No	Yes	No
Maintenance	Very little	High	Low
Thermal efficiency	Very high	Low	High
Space requirement	Less	More	Less
Equipment cost	Higher	Highest	Low
Operational (Availability)	Continuous	Non continuous	Almost continuous
Secondary Scrubber requirement	No	Yes	Yes

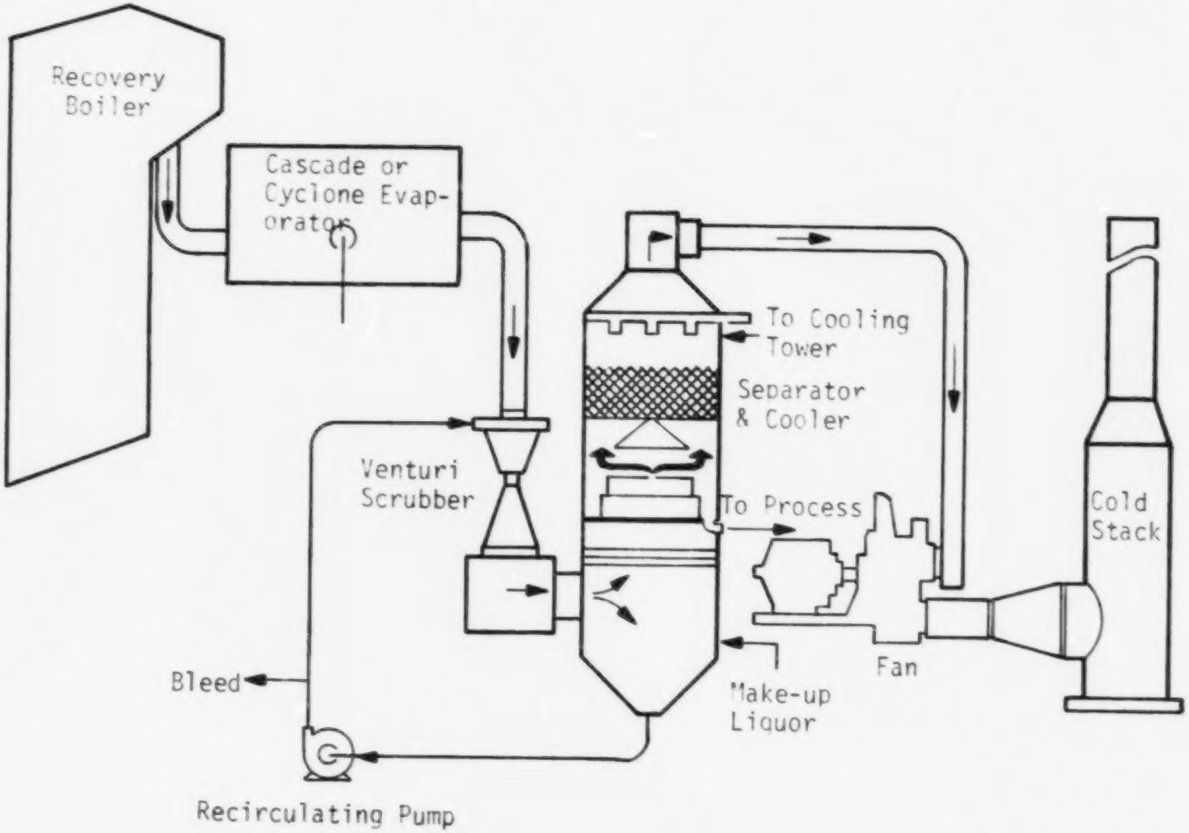

Recovery
Boiler
Cascade or
Cyclone Evap-
orator
To Cooling
Tower
Separator
& Cooler
Venturi
Scrubber
To Process
Cold
Stack
Fan
Bleed
Make-up
Liquor
Recirculating Pump

FIGURE 3-5. SINGLE STAGE VENTURI SCRUBBING SYSTEM

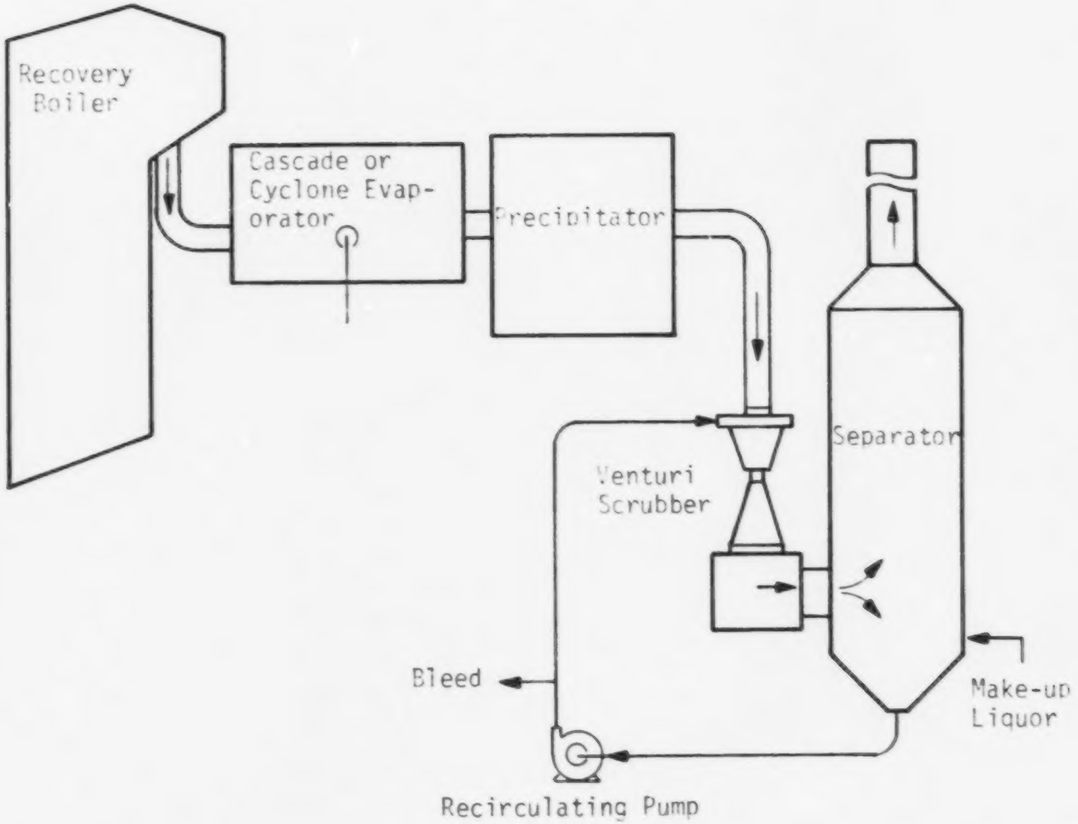

Recovery Boiler
Cascade or Cyclone Evaporator
Precipitator
Venturi Scrubber
Separator
Bleed
Make-up Liquor
Recirculating Pump

FIGURE 3-6. SECONDARY VENTURI SCRUBBING SYSTEM (FOLLOWING PRECIPITATOR)

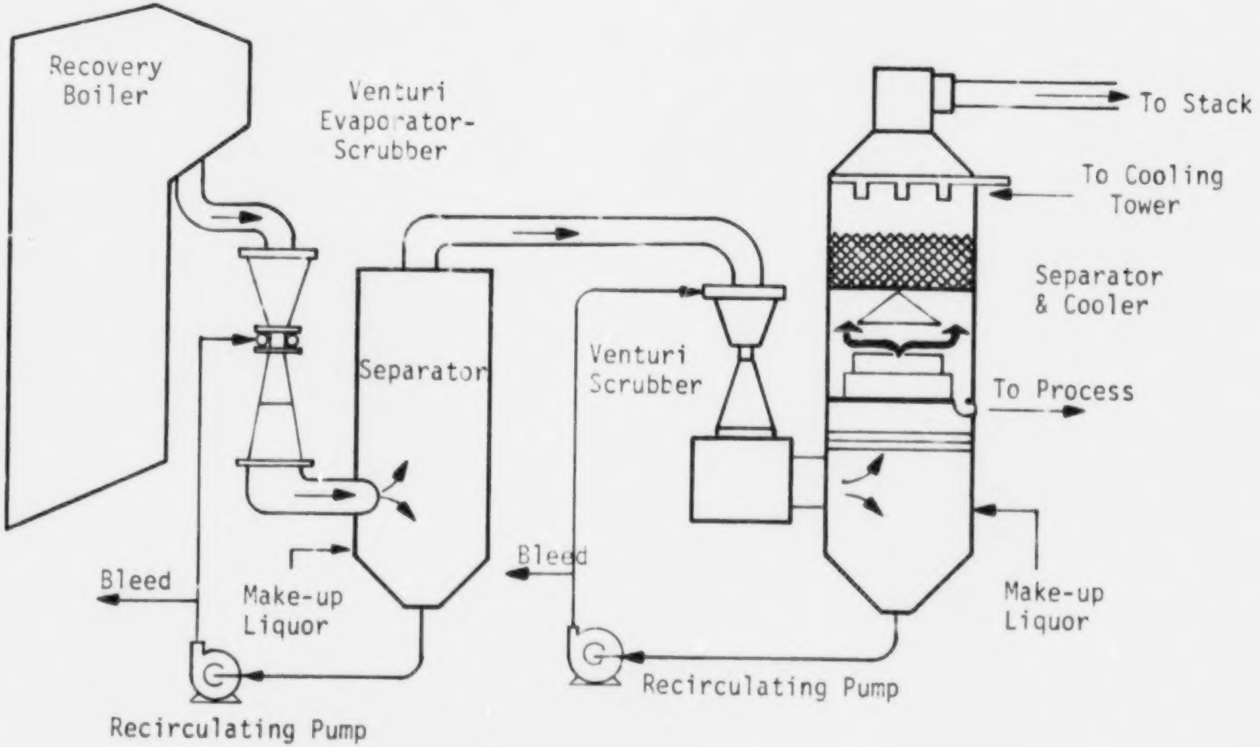

Recovery Boiler
Venturi Evaporator-Scrubber
Separator
Make-up Liquor
Bleed
Recirculating Pump
Venturi Scrubber
Bleed
Recirculating Pump
To Stack
To Cooling Tower
Separator & Cooler
To Process
Make-up Liquor

FIGURE 3-7. SECONDARY VENTURI SCRUBBING SYSTEM
(Following Existing Venturi System)

TABLE 3-3 A

OPERATING PERFORMANCE OF SECONDARY SCRUBBING SYSTEMS

	Cyclonic Scrubber	Venturi Scrubber
Gas temperature		
°F In	300	300
°F Out	160 - 170	160 - 170
Dust loading		
GR/SCF Dry In	0.5 - 1.0	0.5 - 1.0
GR/SCF Dry Out	0.05 - 0.1	0.04
Efficiency %	90	90 - 98
Pressure Drop "WG"	1-3	10 - 15
Liquor Concentration		
% Solids In	0 - 10	0 - 18
% Solids Out	15	30

provide 98 percent efficiency at a pressure drop of 12 to 15 inches W.G., thus an overall efficiency of 98 to 99 percent can be attained.

When the precipitator is taken out, the gases from the evaporator can be diverted to the venturi system. An overall efficiency of 95 %, plus can be attained at a pressure drop of 25 in. w.g. across the scrubber.

When the P-A venturi evaporator-scrubber system is providing only 85 to 90% efficiency at a pressure drop of 35 to 40 in. w.g. and has to be upgraded to obtain an overall efficiency of 99% plus, it should be upgraded by conversion into a two-stage system, as shown in Figure 3-7. The existing separator and fan could be utilized in the converted two-stage system, by transferring the majority of available static pressure to the second stage with only a minimum applied to the first (evaporation) stage. This way, performance equivalent to a two-stage evaporator-scrubber system can be achieved.

3.2.9 RECOVERY FURNACE SYSTEMS WHICH ELIMINATE DIRECT CONTACT BETWEEN BLACK LIQUOR AND FLUE GASES

In the past five years, there have been several applications of the "odor free" recovery boiler in the industry, as manufactured by the two major boiler companies, Babcock and Wilcox (B & W) and Combustion Engineering (C-E). Essentially, the modification developed by both companies avoids direct contact of black liquor with boiler flue gases, as formerly required to achieve liquor concentrations in the 70% solids range.

By eliminating the D-C evaporator, the B & W approach puts more emphasis on the multiple effect evaporator train, which heretofore has been only marginal in raising the solids concentration of weak black liquor. B & W says its improved design can reach 60 to 65% solids, well above the usual minimum of 55% that is required for steady, safe operation of the boiler.

B & W's three main design changes are: additional indirect evaporation stages which uses forced circulation of liquor through the exchangers (due to the higher viscosity of strong black liquor); a revised tube-survace arrangement to offset scaling and poorer rates of heat transfer; and a steam pressure limit of 35 psig. coming into the multiple effect train, so that maximum steam pressure in the first effect (where viscosity is highest) to 8 psig. (Usual practice has been to employ 60 psig. steam, but the lower pressure, notes the company, brings the temperature down to a point where scaling is substantially reduced).

To recover heat from the flue gases, and also to cool gases before admitting them to the electrostatic precipitator, B & W outfits the economizer with approximately three times the surface area of a comparable unit feeding 50% liquor to a direct contact evaporator. The gas temperature at the exit of the enlarged economizer is about 50°F higher than with a direct contact unit. The only advantages claimed for the higher temperatures are reduction of corrosion in the precipitator and less steam plume.

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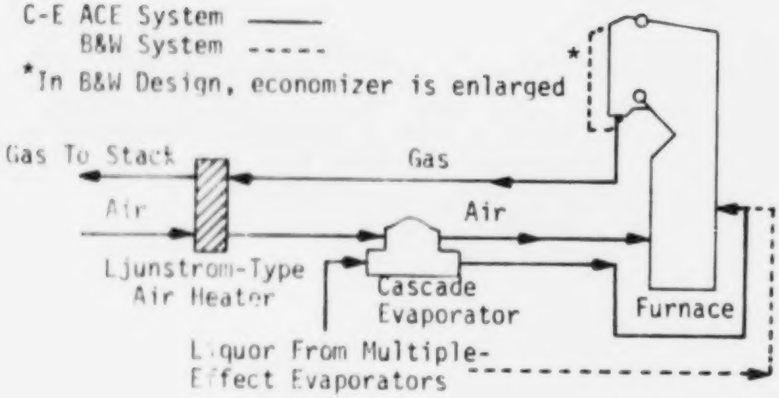
C-E ACE System
B&W System
*In B&W Design, economizer is enlarged
*
Gas To Stack
Gas
Air
Air
Ljunstrom-Type Air Heater
Cascade Evaporator
Furnace
Liquor From Multiple-Effect Evaporators

FIGURE 3-10. COMPARISON OF C-E AND B&W RECOVERY BOILERS SHOWS DESIGN DIFFERENCES WITH OR WITHOUT THE DIRECT-CONTACT EVAPORATOR

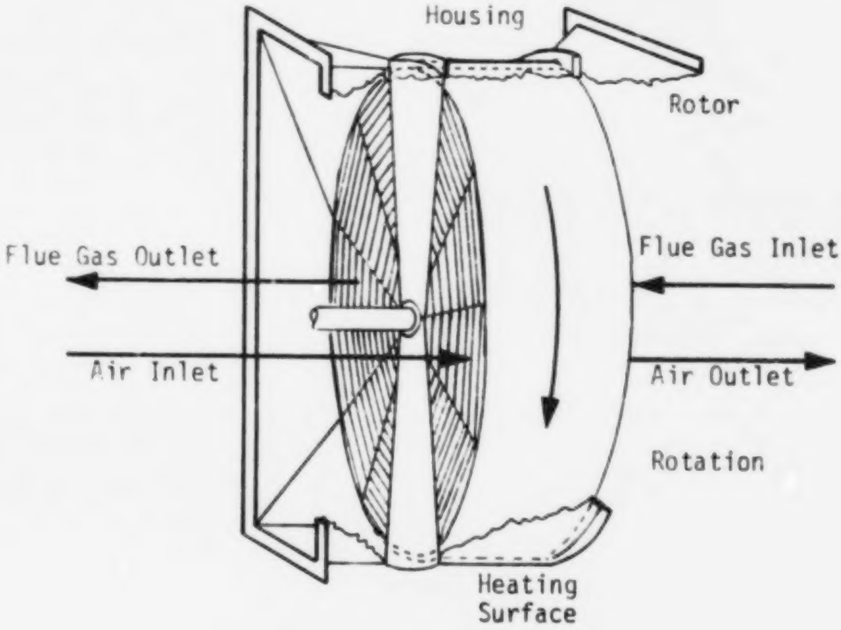
Housing
Rotor
Flue Gas Outlet
Flue Gas Inlet
Air Inlet
Air Outlet
Rotation
Heating Surface

FIGURE 3-11. DETAIL SHOWS THE LAMINAIRE AIR HEATER USED IN THE C-E DESIGN

3.2.11 LIME KILN

The lime kiln is a major source of chemical loss in the form of particulate emissions. The gaseous emissions are not so pronounced. In the lime recovery process, lime is usually lost at various points--some with grits or impurities removed by the slaked lime classifier and some at storage facilities for reburned lime. The major source of loss is the exit gases leaving the kiln. The lime dust escaping with the flue gases is more objectionable than the calcium carbonate and lime lost at the other end of the kiln because it is reactive lime. The major loss of particulate matter from this source is alkaline earth oxides.

The other minor chemical loss which creates an odor problem, is the release of sulfur bearing compounds through exit flue gas. The quantity of odor from lime kiln gases is very, small as compared with other sources in the pulp mill. To understand and develop an odor control system or to minimize the formation and release of odorous compounds, it is necessary to evaluate the sources contributing to odor emission. The possible sources of sulfur compounds are:

1. The degree of washing of lime mud and the filter cake dryness determines the amount of sodium sulfide in the lime sludge. In cases where liquor sulfidity is high and washing poor, as much as 5 pounds of sodium sulfide per ton of pulp production may be present in lime sludge fed to the kiln. The high carbon dioxide and high temperature atmosphere may favor release of hydrogen sulfide and sulfur dioxide according to the following reactions:

   $$Na_2S + SO_2 + H_2O \rightarrow Na_2CO_3 + H_2S$$

   $$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

   The hydrogen sulfide emissions will increase with lowering of kiln exit temperature or oxygen content.

2. A high sulfur content fuel oil used in the kiln as a fuel source results in the release of sulfur dioxide.

3. Where the water supplies are limited and a mill has a tight water balance, the evaporator condensate is used as makeup to the kiln scrubbing system. If the mill does not practice weak black liquor oxidation or stripping of the condensates, this may become a significant odor source.

4. Some mills practice burning of the noncondensible gases released in the digester and evaporation process in the kiln. These gases with high sulfur content are efficiently burned in the high temperature zone.

The use of wet scrubbers, of low sulfur content fuel, and the efficient control of combustion and the proper washing of lime mud will definitely reduce the odorous gases and chemical losses in the form of sulfur dioxide and hydrogen sulfide.

The flue gas leaving the kiln carries an appreciable quantity of dust. The chemical composition of the dust is essentially carbonates and oxides of sodium, calcium and magnesium, sodium sulfate and acid insolubles (consisting of aluminium oxide, iron oxide, silica and others). The amount of chemicals leaving the kiln in the flue gases may range from 5 to over 20 grains/cubic foot. This represents a loss of 10 to 20 tons/day.

To recover these chemicals, the wet scrubber is very widely used. Of the various types, the venturi scrubber in Figure 3-12 has proven to be most efficient. There are about 100 installations throughout the industry. The lime kiln scrubber should be considered as an essential and integral part of kraft chemical and heat recovery process, just as a lime kiln constitutes an integral part of the causticizing and chemical recovery process.

With the use of the efficient venturi scrubber, these chemical losses are reduced by 99% plus. The collection of lime dust is not as difficult as the collection of soda dust. The soda is in the form of very fine fume and requires higher energy for collection. At a total pressure drop of 15 to 17 in. w.g. across the scrubber system, essentially all the lime dust can be recovered whereas only 70 to 80% soda fume is recovered. The sulfur dioxide and hydrogen sulfide will be absorbed efficiently in the venturi type scrubbers. It is believed that better mud washing methods and improved control of lime kiln operation, coupled with the efficient scrubber operation, can result in a totally satisfactory solution to this problem.

The lime kiln scrubber system as in Figure 3-12 consists of a venturi flooded elbow and a cyclonic separator. In the venturi, the scrubbing liquor enters tangentially into the shelf section and swirls down the converging walls. It then hits the lip section in the throat which throws the liquor toward the center thus creating a curtain of liquor across the throat. The dust laden gas enters the venturi through a thimble, accelerates through the convergent section, impacts with the liquor curtain thus shattering it into droplets into which the particulate matter imbeds and is collected. The cleaned gas and liquor enter the flooded elbow. The gas then tangentially enters the cyclonic separator where any entrained liquor is separated. For efficient separation, both the spin height and the vertical velocity are important factors for design. If the separator is not properly designed, carry over of liquor droplets will occur and will result in increased dust loss to the atmosphere.

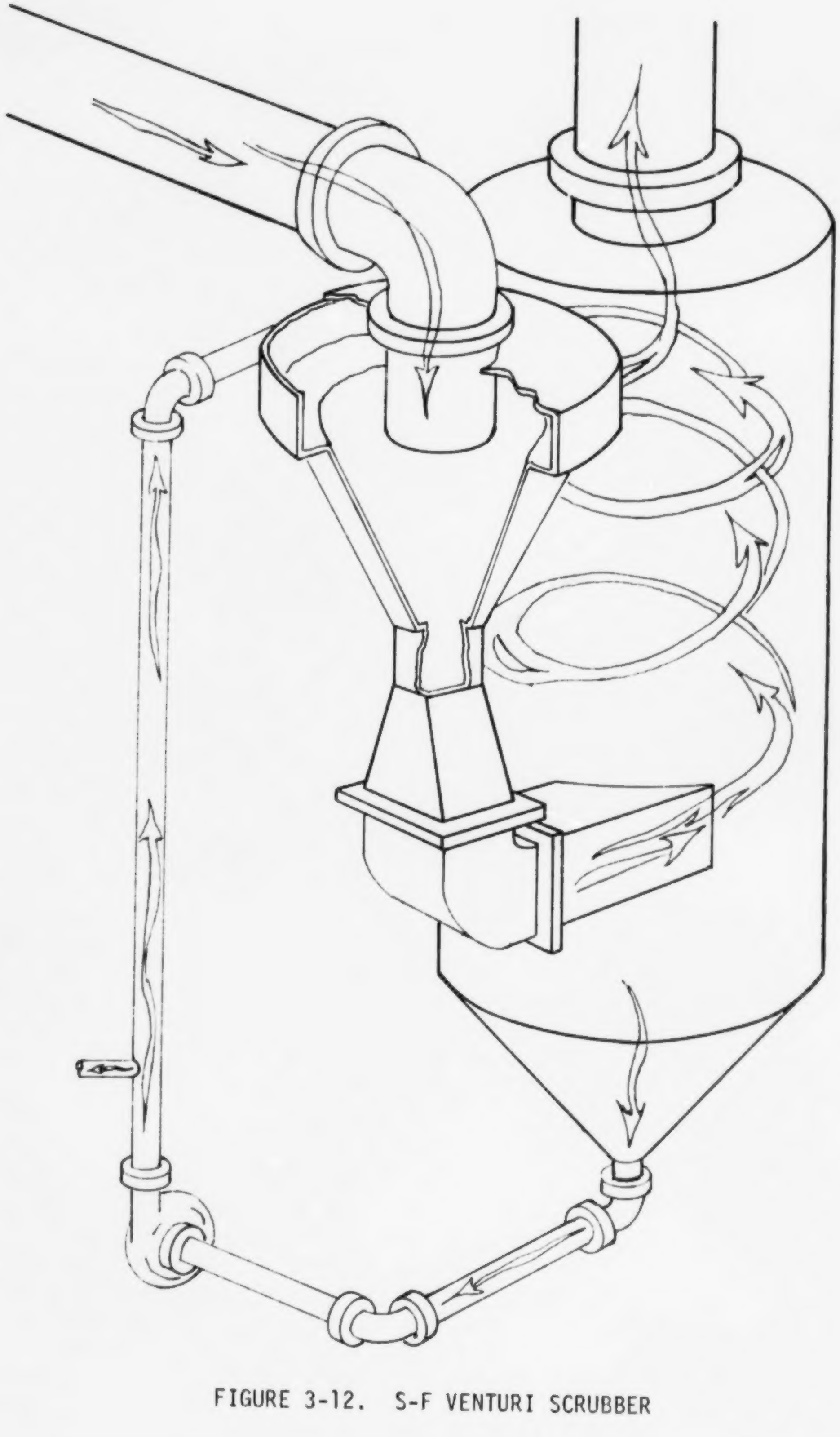

FIGURE 3-12. S-F VENTURI SCRUBBER

The venturi scrubber has also been found to be an effective device for the removal of malodorous gases. The scrubbing solution used in the lime kiln scrubber is alkaline, and the acidic gases such as hydrogen sulfide, sulfur dioxide, etc., will be efficiently absorbed, provided solution pH is maintained in proper range.

3.2.12 THE EFFECT OF PROCESS AND CONTROL EQUIPMENT VARIABLES ON PULP PRODUCTION AND EMISSIONS

The following sections describe process and emission control equipment variables which affect pulp production rates and attendant emission levels for the kraft pulping process.

3.2.12.1 Recovery Furnace System

In the kraft process the more conventional chemical recovery complex consists of the recovery boiler and the direct contact evaporator(s). In the more recent "low odor" recovery systems, the acidic products of combustion from the furnace are not directly contacted with the strong black liquor, thus eliminating the stripping of malodorous reduced sulfur compounds from this unit process.

NCASI studies (18) have identified black liquor solids firing rates, available oxygen supply, adequate residence time in the combustion zone, and turbulence to be important factors in controlling reduced substances lost from the smelting zone of recovery furnaces. In other studies, Thoen et.al. (19) reported that in addition to the above factors, the ratio of primary to secondary air and liquor spray firing patterns were significant factors in controlling emissions from recovery furnaces. In another detailed study, Murray (20) further related the ratio of available air to liquor flow and sulfide content of the fired liquor to reduced sulfur concentrations in recovery furnace exit gases. Smelt bed depths, although not considered to be as important as the previously described variables, can have some effect on both particulate and gaseous emissions from the furnace. In general, the deeper the smelt bed, the greater the loss of both particulate and gaseous materials from the smelting zone.

Black liquor firing rates are directly proportional to pulp production and also have a profound effect on both particulate and gaseous sulfur emissions from the furnace itself. High flue gas velocity, normally attendant to increased liquor firing rates, may cause the carry-up of small droplets of black liquor which have been sprayed into the furnace. The increased flue gas velocity may also entrain additional quantities of the inorganic sodium salts, primarily sodium sulfate and sodium carbonate, which are present in recovery complex emissions.

The direct contact evaporator(s) receiving the furnace gases effectively serves as particulate reduction devices, thus minimizing particulate loadings to the subsequent emission control equipment. Normally, direct contact evaporators will remove approximately 40 to 60 percent of the particulate emissions from the recovery furnace. Particulate emissions from the direct contact evaporator(s) are dealt with most effectively by employing such control devices as electrostatic precipitators and Venturi scrubbers. It is normally more advantageous to control furnace operating conditions to minimize gaseous emissions rather than particulate emissions. However, as a general rule, most operating conditions which result in reduced gaseous emissions also serve to reduce particulate emissions.

Particulate levels in kraft recovery furnace flue gases, prior to reaching a reduction device, normally range from 8.0 to 12.0 grains per standard dry cubic foot of flue gas. The atmospheric emission levels are a function of control device efficiency which is dependent upon the system design. In conventional recovery furnace systems (those with direct contact evaporators), particulate emission control consists of: (a) the contact evaporator; (b) a primary unit which is either a precipitator or a Venturi recovery unit; and (c) in some cases, secondary scrubbers. In newer systems where no flue gas direct contact evaporators are employed, high efficiency (99+%) electrostatic precipitators are used for particulate control almost exclusively. This does not, however, preclude the addition of secondary scrubbers to solve special "snowing" problems. Particulate collection efficiencies for the previously described recovery furnace complex generally range from 85-99+ percent with the higher percentages applying to systems installed within the past few years.

In conventional recovery complex systems, malodorous reduced sulfur compounds may be present in the furnace exit gases and also "stripped" from the black liquor in the direct contact evaporators. Generally, in the absence of black liquor oxidation, the contact evaporators are the major source of malodorous sulfur gas emissions. Sulfide and available alkali content of the black liquor entering the contact evaporators are the major variables in controlling the loss of reduced sulfur compounds from this unit process. Numerous studies have shown that inorganic and organic sulfide stripping is minimized when the measurable sulfide and mercaptide content of the black liquor is below 0.1 grams per liter. Hydrogen sulfide accounts for most of the reduced sulfurs emanating from this operation, although there can be methyl mercaptan, dimethyl sulfide, and dimethyl disulfide present. These organic sulfur compounds seldom exceed ten percent of the H_2S present and normally are not measurable at all.

In well controlled recovery complex systems, atmospheric emission levels of reduced sulfur compounds may be as low as 1.0 parts per million (ppm) by volume to several hundred ppm. The wide range of emission levels is a function of the aforedescribed process and control equipment variables.

Historically, there has been little concern for the SO_2 generated in a kraft recovery furnace. In conventional kraft recovery furnace system designs concentrations are substantially reduced when furnace exhaust gas passes through the contact evaporator. After the contact evaporator they are characteristically below that existing from the combustion of fossil fuels containing 0.5 percent sulfur, i.e. less than 300 ppm, usually between 50 and 150 ppm. Concentrations of SO_2 in recovery furnace exhaust gas range from less than 50 to as high as 700 or 800 ppm. The factors responsible for this range of concentration are not well identified. Blue and Llewellyn (21) as well as results of currently unpublished studies indicate that SO_2 generation in kraft recovery furnaces is a function of several variables. One is cooking liquor sulfidity, and indirect measure of the soda and sulfur ratio in black liquor fed to the furnace. Others include smelt bed depth, manner in which liquor is sprayed into the furnace, ratio of primary to secondary combustion air and possibly temperature within the furnace itself. As previously stated, the higher concentrations are of limited practical concern except in those recovery system designs which eliminate the contact evaporator.

3.2.12.2 Lime Kilns

The lime kiln is a major source of chemical loss in the form of particulate emissions. The gaseous emissions are not so pronounced. In the lime recovery process, lime is usually lost at various points--some with grits or impurities removed by the slaked lime classifier and some at storage facilities for reburned lime. The major source of loss is the exit gases leaving the kiln. The lime dust escaping with the flue gases is more objectionable than the calcium carbonate and lime lost at the other end of the kiln because it is reactive lime.

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   The hydrogen sulfide emissions will increase with lowering of kiln exit temperature or oxygen content.

2. The high sulfur content fuel oil used in the kiln as a fuel source results in the release of sulfur dioxide.

3. Where the water supplies are limited and a mill has a tight water balance, the evaporator condensate is used as makeup to the kiln scrubbing system. If the mill does not practice weak black liquor oxidation, this may become a significant odor source.

4. Some mills practice burning of the noncondensable gases released in the digester and evaporation process in the kiln. These gases with high sulfur content are efficiently burned in the high temperature zone.

The use of wet scrubbers, of low sulfur content fuel and the efficient control of combustion and the proper washing of lime mud will definitely reduce the odorous gases and chemical losses in the form of sulfur dioxide and hydrogen sulfide. A typical lime kiln scrubbing system is shown in Figure 3-13.

The flue gas leaving the kiln carries an appreciable quantity of dust. The chemical composition of the dust is essentially carbonates of sodium, calcium and magnesium, sodium sulfate and acid insolubles (consisting of aluminum oxide, iron oxide, silica and others). The amount of chemicals leaving the kiln in the flue gases may range from 5 to over 20 grains/cubic foot. This represents a loss of 10 to 20 tons/day (for a 400 TPD mill).

Factors which affect reduced sulfur emissions from the kiln proper have been identified as stack gas oxygen content, design dimensions, operating temperature, and effectiveness of the lime mud washer. Those operating parameters which have been identified as being responsible for the reduced sulfur contribution from the scrubbing system include make-up water source and recirculation rate, pH of the scrubbing solution, and the sulfide content of the particulate matter.

Minimum emission rates which can be consistently obtained through the optimum control of these variables have not yet been fully established. Current findings indicate the emission concentration can be maintained at less than 50 ppm or 0.25 pounds of sulfur per ton of air dried pulp. While kiln operating variables which affect the emission of hydrogen sulfide have been identified, minimum emission rates which can be consistently attained through controlled operation have not been fully established.

Hydrogen sulfide can be emitted from two distinct and separate points which are:

1. the lime kiln proper

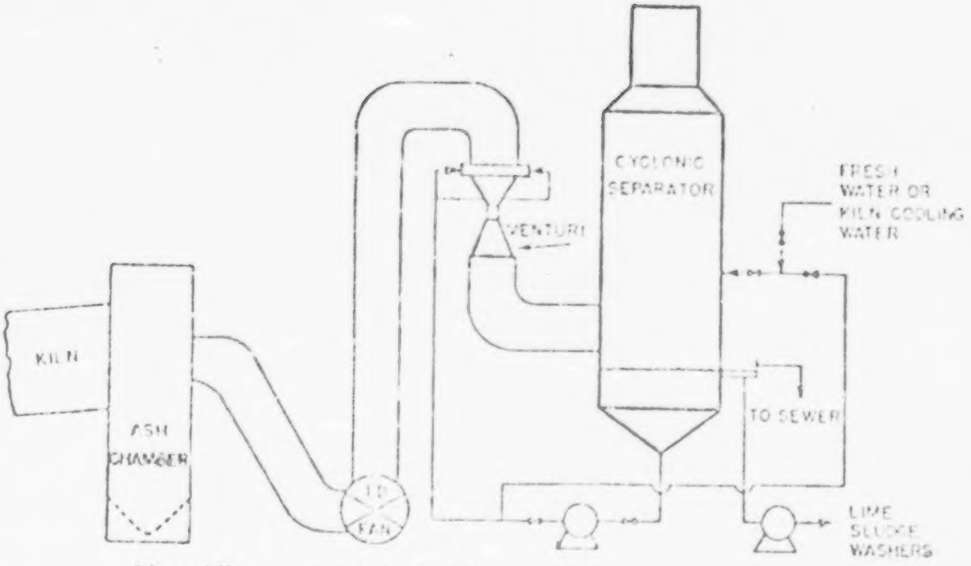
2. the particulate control scrubber

Factors which affect the concentration of reduced sulfur in the exit gas from the lime kiln include:

1. oxygen content of the exit gas,

2. length to diameter ratio of the kiln,

3. sulfide content of the lime mud,


KILN
ASH CHAMBER
ID FAN
VENTURI
CYCLONIC SEPARATOR
FRESH WATER OR KILN COOLING WATER
TO SEWER
LIME SLUDGE WASHERS

Lime kiln venturi scrubber system.

FIGURE 3-13

4. cold-end operating temperature,
5. burning of green liquor dregs.

Operating variables of the particulate control scrubber which govern the contribution of hydrogen sulfide include:

1. source of scrubber make-up water,
2. recirculation rate,
3. pH of the scrubbing solution,
4. acid liberated sulfide content of the particulate collected.

Minimum hydrogen sulfide concentrations in the stack gas of individual kilns have been measured at oxygen contents of 3.5 to 4.0 percent for units operated under stable conditions. The hydrogen sulfide values recorded have varied from 10 ppm to about 100 ppm for properly operated kilns. The higher concentrations were associated with "so-called" long kilns operated on lime mud of high sulfide content. A typical hydrogen sulfide vs. oxygen content curve is shown in Figure 3-13 A.

Long kilns are characterized as units with lengths of 25 diameters or more and short kilns as units with lengths of 20 diameters or less.

The gross effect of lime mud sulfide content on kiln proper hydrogen sulfide emission rates is presented in Table 3-4 (22). Operating conditions during intervals II and III on two separate trials on one kiln were similar, as was the hydrogen sulfide emitted. During interval IV, the only operating variable changed was the removal of green liquor dregs from the kiln lime mud feed. The corresponding reduction experienced in the hydrogen sulfide emission was about 40 percent.

Particulate emissions from the lime kiln consist of the sodium salts, calcium carbonate, calcium sulfate, calcium oxide, and insoluble ash. The presence of the sodium salts may be accounted for by the sublimation-condensation process, and by dust entrainment within the kiln. However, neither calcium carbonate, nor calcium oxide will vaporize at temperatures within the kiln and the presence of calcium carbonate and calcium sulfate must be explained by the entrainment of the calcium carbonate and calcium oxide. The particles of calcium oxide may react with either

FIGURE 3-13 A

TOTAL REDUCED SULFUR VS. EXCESS OXYGEN

LIME KILN

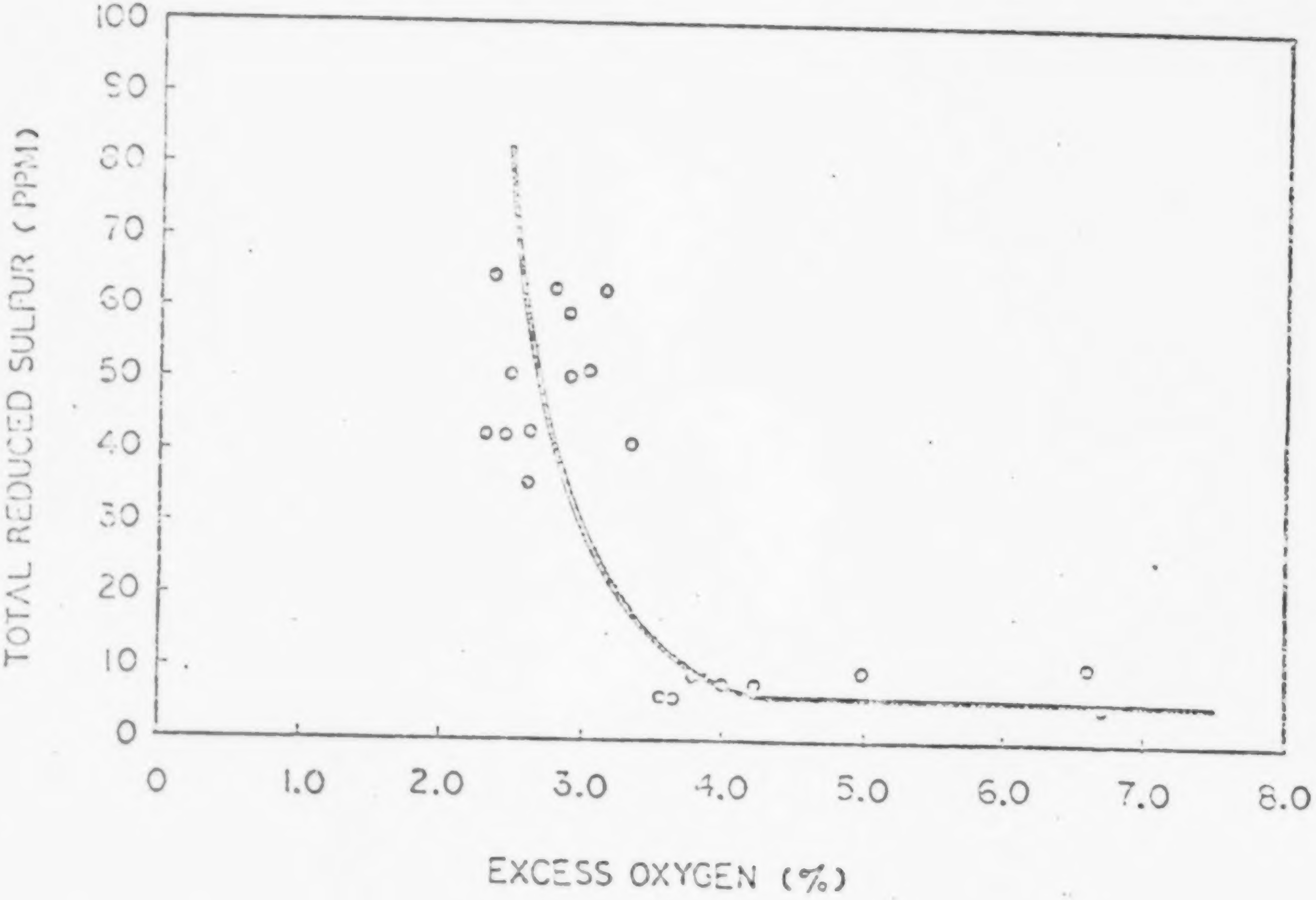


TABLE 3-4

LIME KILN EMISSIONS (Prior to Particulate Control Device) AS RELATED TO OPERATIONAL VARIABLES (22)

Interval i	Stack Gas SO_2 Content	Burnings Dredge	H_2S	
			ppm	Lbs S/Ton
I	0	Yes	804	2.9
II	2.8	Yes	506	1.7
III	2.4	Yes	463	1.5
IV	2.8	No	243	0.9
V	4.0 - 7.0	No	60 - 86	0.2 - 0.3

carbon dioxide or sulfur dioxide within the kiln to yield the appropriate calcium salt. Calcium carbonate may react with the sulfur dioxide and then oxygen to yield calcium sulfate.

$$CaO + CO_2 \rightarrow CaCO_3$$

$$CaO + SO_2 \rightarrow CaSO_3$$

$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$$

$$CaSO_3 + 1/2O_2 \rightarrow CaSO_4$$

The particulate emissions from the lime kiln (before the control equipment) are about one-fourth the emissions from the recovery furnace but are still significantly large. However, the relatively low gas flow rates through the lime kiln allow installation of moderately priced high efficiency wet scrubbers which can reduce particulate emissions to low levels. At the present time, most lime kilns are equipped with wet scrubbers whose efficiencies range from 80 to 99 percent on the calcium salts. The particulate emissions from the lime kilns whose scrubber efficiencies are in the lower part of the range may be significant.

Other than controlling the rate of material output there appears to be no well defined method of controlling the particulate emission for the lime kiln through manipulation of operating variables.

The previously described particulate control system employed on most lime kilns can be a source of reduced sulfur losses dependent upon the source of scrubbing water and the recirculation rate. Although the collected particulates are alkaline, the kiln exit gases are rich in carbon dioxide and, therefore, caused a pH drop in the scrubbing medium. In these cases, soluble sulfides in the scrubbing liquid may be evolved as hydrogen sulfide. This potential condition then dictates the necessity of utilizing sulfide free source water for the scrubbing system.

3.2.12.3 Smelt Dissolving Tank

Both particulate material and reduced sulfur compounds are present in the vented gases from smelt dissolving tanks. Particulates are primarily caused by the entrainment of large particles in the vent gases. Because of the violent reactions taking place when the molten smelt from the furnace is discharged into the tank, the turbulence created will "splash" water droplets which contain both dissolved and undissolved inorganic salts above the liquid surface of the tank. Therefore, due to the high temperature of the offgases, the small particles, now in suspension, are carried out with the gas stream.

Some reduced sulfur compounds are formed by reactions in the tank and others are distilled from the make-up water, usually weak filtrate from the lime mud washer, added to the dissolving tank.

Operational variables most influential on these emissions are (a) rate of molten smelt discharge from the recovery furnace and (b) source of make-up water utilized. The shatterjet system utilized on the furnace smelt spouts can also have a significant effect on particulate emissions from this source.

Wire mesh mist eliminators are currently the most used emission control devices employed on smelt tank vents. However, more recently, wet scrubbing systems, including packed columns, are now being installed in many places. These scrubber/absorption systems can be effective on both particulates and reduced sulfur emissions when the proper scrubbing medium is used.

3.2.12.4 Multiple Effect Evaporators

The kraft process utilizes multiple effect evaporation to concentrate weak black liquor (spent cooking liquor) washed from the pulp. Removal of large amounts of water from the liquor is necessary to facilitate combustion of the dissolved organic material in the recovery furnace. The liquor is concentrated in the multiple effect evaporators from a solids content of 12-18% to 40-55% (25).

Most kraft mills utilize long-tube vertical shell-and-tube type evaporators. The weak black liquor is fed to the tube side of the latter evaporation effects and steam is supplied to the shell side of the first effect. The liquor proceeds through the tube side of each effect from last to first, being heated in each by condensation of the vapor driven off the boiling liquor in the tube side of each preceding effect.

Evaporated water vapor from the last effect of the set is condensed in one of two types of condensers: (a) direct contact barometric condensers, and (b) surface condensers with steam ejectors. The condenser must remove vapor fast enough to create a vacuum in the vapor space of the last effect. Each type of condenser is equipped with a small steam ejector to remove noncondensibles.

The emissions from the multiple effect evaporators are non-condensible reduced sulfur gases which are vaporized or stripped during the boiling. These non-condensible gases, with vapors created during boiling, pass to the heating element of the following effect. The reduced pressure in the later effects will result in a higher evolution of the reduced sulfur compounds. This increased evolution and the steam stripping of the reduced sulfur compounds are responsible for the emissions from this source.

In order to eliminate an accumulation of non-condensible gases in the heating element each heating element is provided with a gas vent. The vents from the heating elements that are under a pressure greater than atmospheric are vented to its vapor head. The vents from the heating elements under a vacuum are usually valved to a common header going directly to either a barometric or surface condenser. The condenser type influences the relative emissions of TRS compounds from this source as indicated in the following table (limited data):

	Emissions (lb/ADT)			
Condenser Type	H_2S	Methyl Mercaptan	Di-methyl Sulfide	Di-methyl Di-Sulfide
Surface	4.80	1.44	0.35	0.62
Barometric (with loss at noncondensible jet)	0.04	0.03	0.04	0
Barometric (losses from hot well)	0.13	0.20	0.14	0.02

Sulfidity and pH of the liquor tend to be controlling factors in the quantity of reduced sulfur compounds emitted. Although black liquor oxidation can reduce the TRS emissions significantly, the residual concentrations are such that further processing of non-condensibles is desirable.

The most common practice, in cases where treatment of these non-condensibles is employed, is to combine these non-condensible gases with the digester blow and relief gases and treat in the same manner as described in section 3.2.12.5.

3.2.12.5 Digester-Relief and Blow

Digester systems employed in the kraft process consists of the batch and continuous types previously described.

Although no particulates are generated from these operations, the relief and blow gases can be the largest potential source of reduced sulfur emissions within the kraft mill. This is mainly due to the fact that most of the malodorous organic sulfur compounds from the kraft process are primarily formed during the digestion of the wood chips. Further, their first opportunity to "escape" comes during the cooking cycle via the relief gases and at the end of the cooking cycle through the blow gases.

Where turpentine recovery is employed, the relief gases are normally passed through turpentine recovery systems where the condensible fractions of the gases are removed. The non-condensible fractions may then be vented to the atmosphere or a control system for further treatment. These non-condensible gases are mainly made up of methyl mercaptan, dimethyl sulfide and dimethyl disulfide.

Blow gases are released at the end of the cooking cycle and, in batch systems, normally pass through a blow-heat recovery system which is relatively ineffective insofar as removal of organic sulfur compounds is concerned. In batch digester systems, the blow-heat recovery tank can be an intermittent, but significant source of malodorous sulfur emissions.

Several operating variables affect both production and sulfur gas emissions from these operations. The most important of these as they relate to emissions are (a) cooking liquor sulfidity (b) duration of cook (c) wood species and (d) degree (severity) of the cook which is related to a,b, and c and the desired yield.

Treatment methods utilized to dispose of the malodorous non-condensible blow and relief gases include thermal oxidation, chemical oxidation and chemical absorption. The most prevalent methods currently in use are a combination of chemical absorption followed by thermal oxidation, most commonly in the lime kiln. As previously stated in section 3.2.12.2 thermal oxidation in the lime kiln virtually eliminates malodors produced by these reduced sulfur compounds. Burning the gases is accomplished in the lime kiln, or a special separate incinerator (23). In burning, care must be taken to avoid the occurrence of explosive mixtures. In a batch digestion system, the problem of preventing large surges of gas to the burning device arises. Gas surge capacity is provided by using large spherical tanks equipped with a movable non-porous diaphram (24), or conventional gas holders. Burning can be a very effective technique for disposal of these gases. Data in the section on lime kilns illustrate this point.

Scrubbing the gas stream with a sodium hydroxide solution offers a partial control method for digester emissions. Effectiveness is limited to H_2S and methyl mercaptan. Some mills use such scrubbers for preliminary treatment of gases before burning them. Three objectives are achieved: (a) some sulfur is recovered, (b) steam is condensed, and (c) turpentine vapors and mists are removed, mitigating an explosion hazard.

Scrubbing with chlorine solutions is practiced in some mills. In the case of bleached kraft mills, chlorine-containing effluent from the bleach plant may be used to scrub the gases. It is necessary that residual chlorine be present at all times in these effluents to maintain the effectiveness of this technique, which is of limited effectiveness at best.

3.2.12.6 Brown Stock Washer Systems

Brown stock washer systems are commonly characterized as high volume-low concentration sources of reduced sulfur compounds. No particulate material is generated from these sources.

Operational variables which affect production and atmospheric emissions include (a) liquor sulfidity (b) pulp flow rate (c) wood species (d) wash water source and (e) storage time in blow tanks (26).

Emissions from the brown stock washers arise primarily from the vaporization of the volatile reduced sulfur compounds. No chemical reactions are believed to take place. However, there is a shift in the equilibrium for hydrogen sulfide and methyl mercaptan. Since the washer water normally has approximately a neutral pH, the dilution of the liquor by the water will cause a lowering of the liquor pH to approximately 10.0. This pH is below the equilibrium point for methyl mercaptide ion and results in a corresponding shift to methyl mercaptan gas. The lower pH will also cause an increase in the concentration of dissolved hydrogen sulfide. However, the equilibrium point of H_2S (8.0) will not be reached.

The composition of these sulfur gases is almost exclusively organic sulfur compounds made up of methyl mercaptan, dimethyl sulfide and dimethyl disulfide.

Control of these emissions is not commonly practiced at the present time stemming primarily from the difficulty and expense of treating the high volume-low concentration sources. However, newer installations are venting these gases to the recovery furnaces for utilization as a source of combustion air. There is a scarcity of available data regarding the effectiveness of this practice in the overall odor reduction of kraft pulp mill operations.

Measured emissions from these sources range between 0.01 and 0.6 with a mean of 0.1 pounds of total reduced sulfur (as H_2S) per ton of air dried pulp (26).

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3.3 DESCRIPTION OF THE NSSC PROCESS

This process is mainly used for the production of a high yield pulp having a high crush strength, important for making corrugated board. In addition, it utilizes hardwood species that are not readily adaptable to the other processes. Coniferous woods are considered less desirable for the NSSC process because of a higher chemical comsumption during cooking, high lignin content for a given yield, and high energy requirements for refining.

Recovery of chemicals from the spent liquor is not practiced at the majority of mills and, therefore, may create a water pollution problem. Incineration of the liquor may, in turn, create an emission problem because of sulfur dioxide emission from the incinerator and will depend on the degree of sulfur dioxide recovery.

Neutral sulfite semichemical pulping is basically a two-stage process. It involves:

1. A mild chemical treatment of the wood chips in the presence of a neutral chemical solution within a digester and followed by
2. A mechanical treatment, called defibering, to disintegrate the wood chips into pulp.

It derives its name "neutral sulfite" from the fact that the solution containing the cooking chemicals, consisting of sodium sulfite and sodium carbonate, is maintained above a pH of 7.0. Aqueous solutions of sodium sulfite are basic but during digestion wood chips release organic acids which if not neutralized will acidify the cooking liquor. Alkali, usually sodium carbonate, is added to the cooking liquor to neutralize the organic acids, primarily to reduce the corrosiveness of the liquor. The higher pH retards hydrolysis of carbohydrates, producing higher yields of stronger pulp; but increases bleaching costs because a darker pulp is produced. The name "semichemical" is given because all of the cementing material is not completely removed by the chemical reaction and some mechanical disintegration is required to separate the fibers. Because some of the cementing material remains with the fibers it follows that the "yield" for this process is higher than for a conventional full-chemical pulping process. Semichemical pulping may produce yields of 60 to 80 percent.

Various types of semichemical pulps are produced by the acid sulfite, neutral sulfite, kraft, soda and cold soda pulping processes. The major process difference from conventional chemical pulping lies in the use of lower temperatures, more dilute cooking liquor or shorter cooking time and mechanical disintegration. Semichemical processes can be categorized as alkaline or acid.

The NSSC process varies somewhat from mill to mill. Some mills recover heat and chemicals from the spent liquor, others dispose of spent chemicals through ponding or other means, including blending with kraft black liquor. This chapter will contain discussions relative to the most pertinent operations currently utilized.

The cooking process is carried out in either batch or continuous digesters. Steam maintains the temperature and pressure of the cook within certain limits depending on the end use of the pulp. During this cooking stage odorous gases are created within the digester. The digester may be partially vented continuously throughout the cook. This serves to remove carbon dioxide from the system and thus helps maintain a high pH in the cooking liquor. At the completion of the cooking cycle, residual pressure within the digester is used to discharge the entire contents of the batch digester into a blow tank. Waste gases, containing the odorous compounds formed in the digester, are usually vented to the atmosphere.

At the completion of the cooking cycle, the internal pressure within the reactor is used to discharge the softened chips to a holding vessel known as the blow tank. The waste gases are usually passed through a condenser to remove steam and other condensible vapors.

After excess liquor is separated by draining, pressing, or washing, the softened chips are reduced to pulp through mechanical treatment in equipment such as rod mills or rotating disc refiners. The pulp is then diluted and usually pumped to multistage drum filters where counter-current washing with water is carried out to remove the spent liquor from the pulp. Other means for washing the pulp are available and are used by some mills. The resultant filtrate is termed weak black (spent) liquor. The washed pulp is then upgraded to the degree desired in subsequent processing steps and ultimately utilized in the production of paper products.

3.3.1 CHEMICAL RECOVERY OR DISPOSAL METHODS

Over the years and up to the present, five different methods have been utilized in disposing of or recovery of the spent liquors from NSSC pulping operations. These five methods consist of 1) dumping the effluent with no recovery, 2) mixing with kraft black liquors for subsequent processing, 3) cross-recovery integrated with a kraft mill,

4) partial or complete recovery utilizing a kraft type recovery boiler or smelter, and 5) fluidized bed recovery system. The first method is obviously no longer considered because of pollution abatement laws and operating economics. For this reason, this method will not be further discussed. A schematic diagram of this operation is depicted in Figure 3-14.

3.3.1.1 Disposal By Mixing With Kraft Liquors

If a kraft system is adjoining, the NSSC spent liquor can be mixed with the spent kraft liquor, up to a limiting percentage, and burned in the recovery furnace. Formerly, the ideal ratio was about three parts kraft pulp to one part NSSC pulp. However, increasingly stringent emissions controls have reduced the salt cake losses from kraft mills to the point that the chemicals recovered from one ton of NSSC pulp production will provide sufficient make-up for eight tons of kraft production. The recovered chemicals are used entirely in the kraft system. Emissions of both sulfur dioxide and hydrogen sulfide may be increased from the kraft recovery furnace when NSSC liquor is added. This is primarily due to the fact that the NSSC liquor is more acid than kraft liquor. Most of the increased hydrogen sulfide losses are, therefore, from the direct contact evaporator.

3.3.1.2 NSSC Cross Recovery With Kraft Recovery Operation

A second class of process involves recovery of NSSC cooking liquor via a cross recovery system in conjunction with a kraft mill, as indicated in Figure 3-15. There are several processes in this class (Tampella, Olinkraft, e.g.). These systems generally recover sodium carbonate from kraft green liquor by crystallization and add sulfur by absorbing sulfur dioxide produced by a sulfur burner. The economics of this process depend upon efficient recovery of gases and liquors at each stage in the operation and usually air emissions from these devices are minimal.

NSSC black liquor from the pulp mill is accumulated in a large storage tank, from where it is processed through a triple-effect evaporator. The heavy liquor, at 52 percent solids, is mixed with strong black liquor from the kraft mill, and the combined stream is run through the existing oxidation system (if available) followed by burning in the existing recovery boiler. The semichemical liquor preparation system functions as follows. Clarified green liquor from the causticizing plant is sent to a crystallizer, where it is cooled to promote crystallization of Na_2CO_3. A centrifuge recovers the carbonate crystals, while the filtrate is sent back to the kraft green liquor system. This basic scheme is illustrated in Figure 3-16.

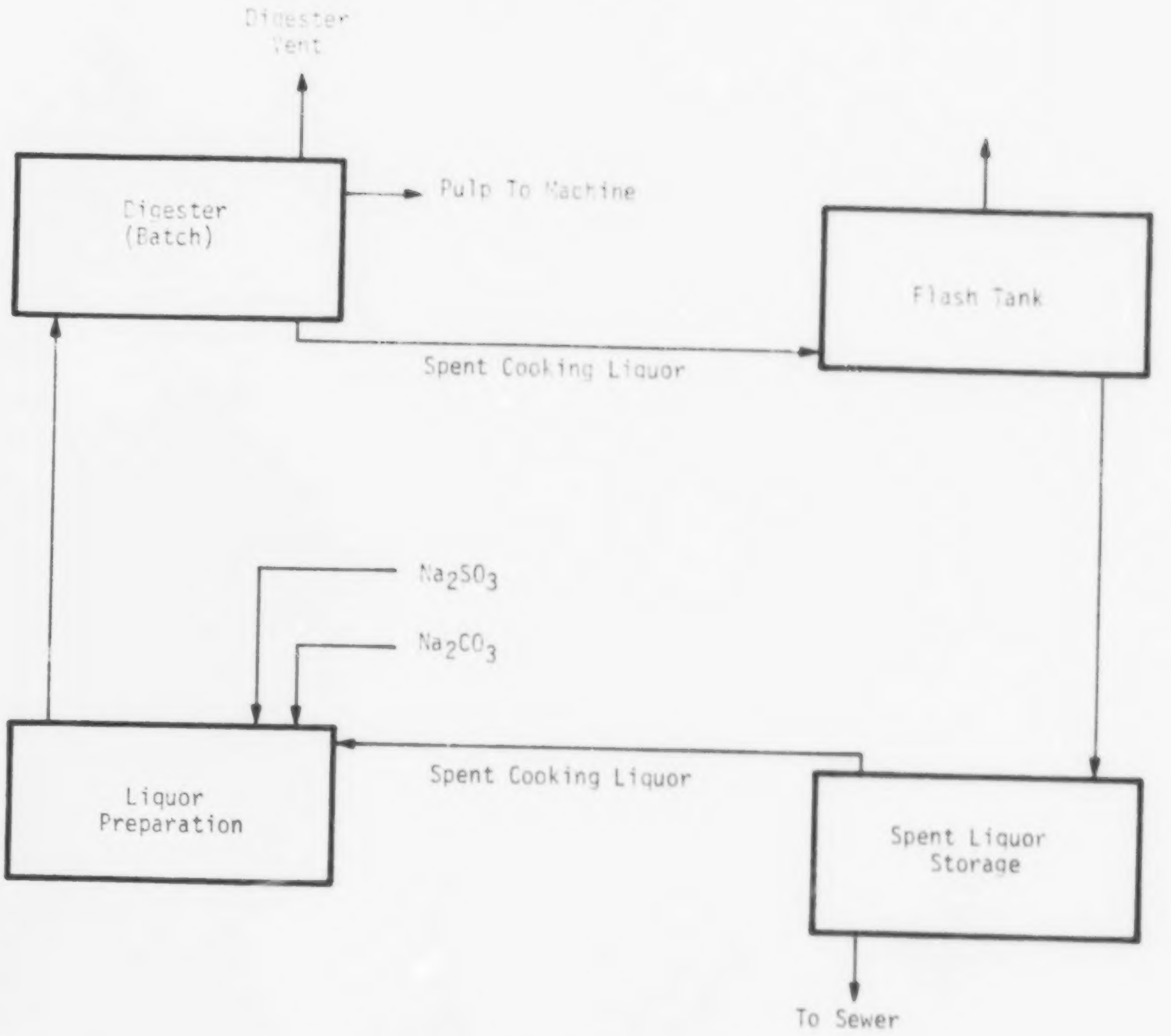

Digester
Vent
Digester
(Batch)
Pulp To Machine
Flash Tank
Spent Cooking Liquor
Na_2SO_3
Na_2CO_3
Liquor
Preparation
Spent Cooking Liquor
Spent Liquor
Storage
To Sewer

FIGURE 3-14. SCHEMATIC DIAGRAM OF NSSC PROCESS WITH NO CHEMICAL RECOVERY

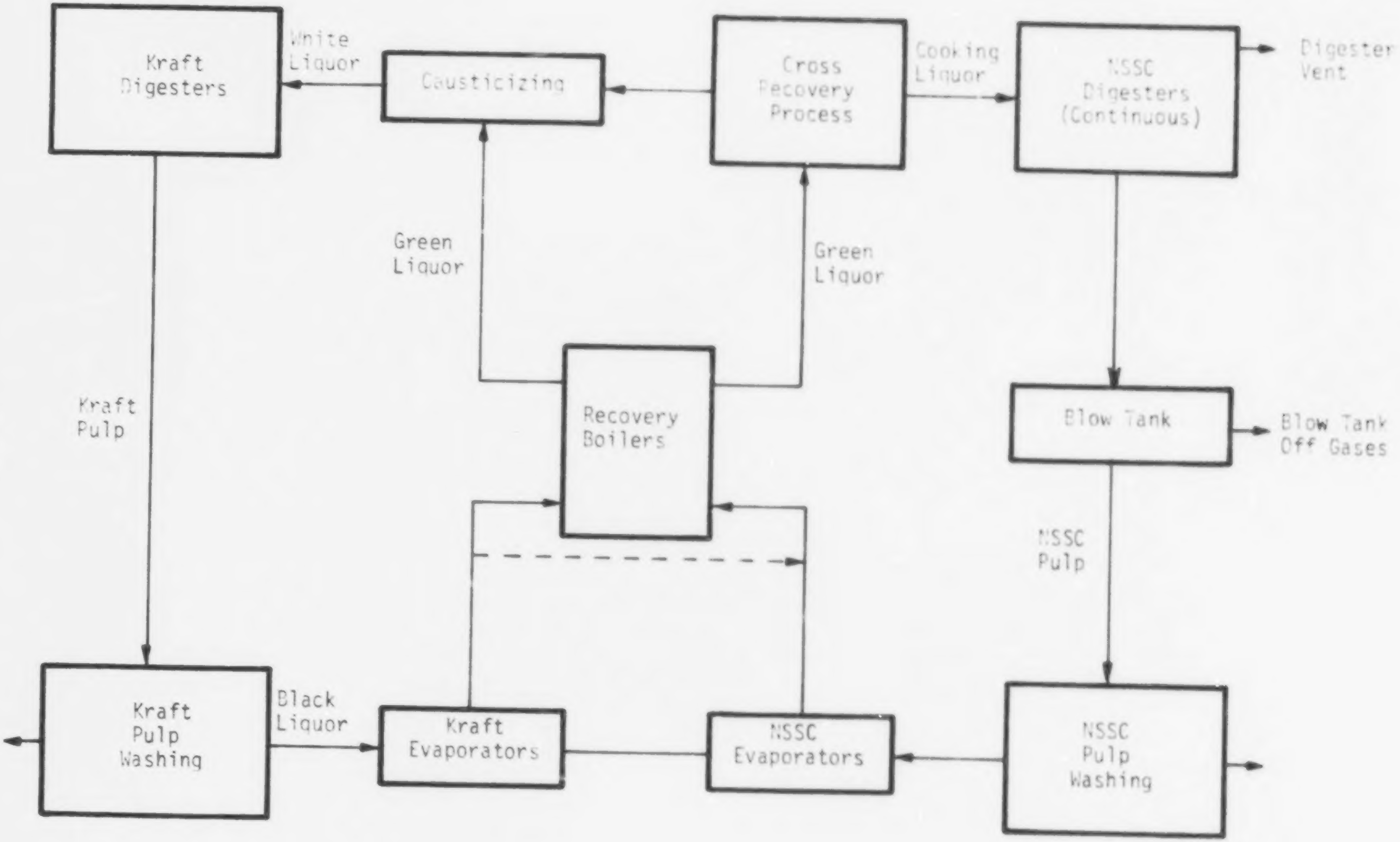

Kraft Digesters
White Liquor
Causticizing
Cross Recovery Process
Cooking Liquor
NSSC Digesters (Continuous)
Digester Vent
Green Liquor
Green Liquor
Recovery Boilers
Kraft Pulp
Blow Tank
Blow Tank Off Gases
NSSC Pulp
Kraft Pulp Washing
Black Liquor
Kraft Evaporators
NSSC Evaporators
NSSC Pulp Washing

FIGURE 3-15. SCHEMATIC DIAGRAM OF CROSS RECOVERY SYSTEM FOR REGENERATING NSSC COOKING CHEMICALS

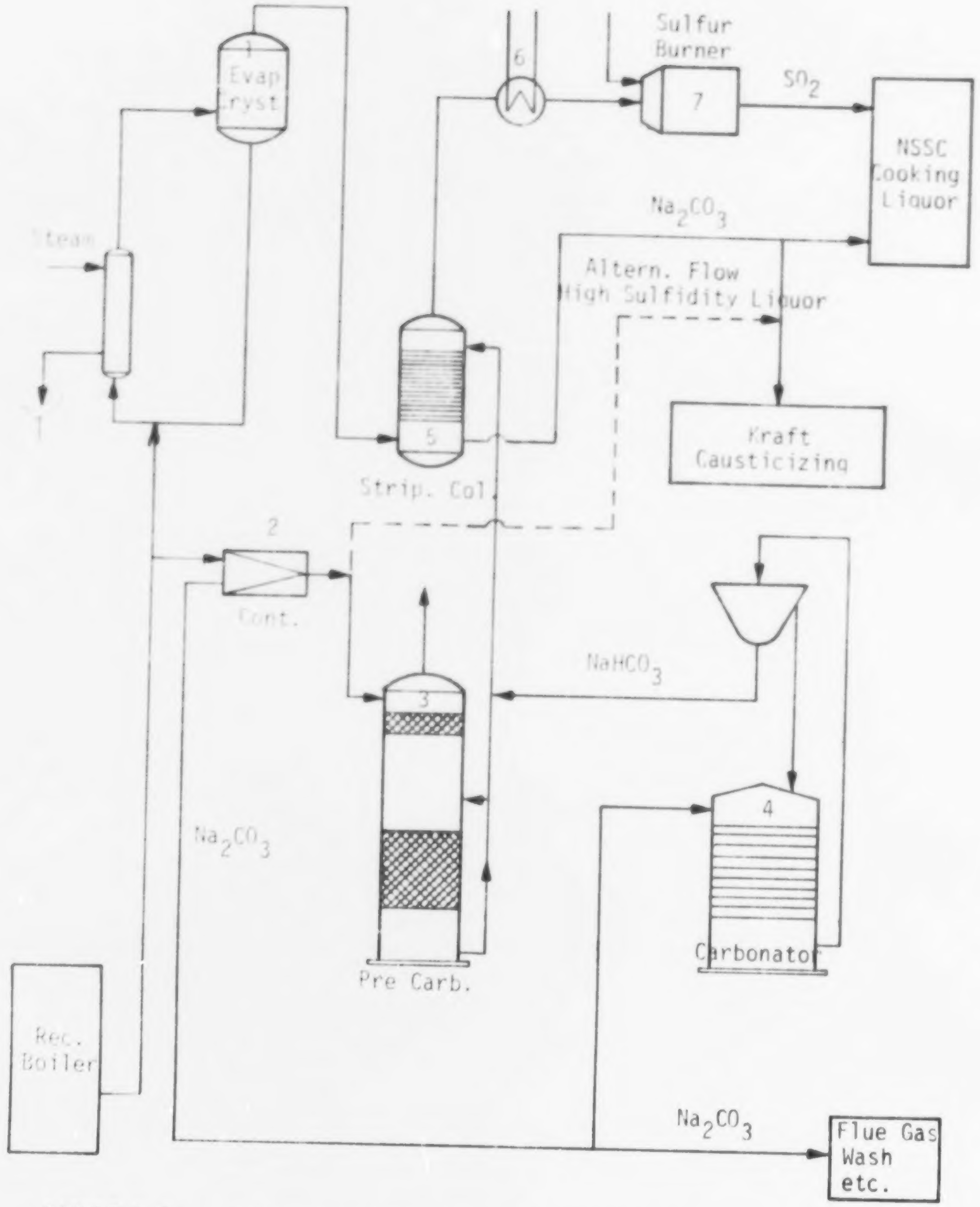

1
Evap
Cryst
Steam
6
Sulfur
Burner
7
SO$_2$
NSSC
Cooking
Liquor
Na$_2$CO$_3$
Altern. Flow
High Sulfidity Liquor
5
Strip. Col.
Kraft
Causticizing
2
Cont.
NaHCO$_3$
3
Pre Carb.
4
Carbonator
Na$_2$CO$_3$
Rec.
Boiler
Na$_2$CO$_3$
Flue Gas
Wash
etc.

FIGURE 3-16. FLOWSHEET OF THE TAMPELLA PROCESS OF SODIUM SULFITE CHEMICALS RECOVERY, WHICH CONVERTS GREEN LIQUOR CHEMICALS INTO SULFITE COOKING LIQUOR

Subsequently, molten sulfur is burned in an appropriate system to produce SO_2. The SO_2 is combined with the Na_2CO_3 solution in an absorption tower. Gas emissions from the liquor preparation and recovery system are run through a fume scrubber before discharge to the atmosphere.

The above processes are convenient where the NSSC mill is operated in conjunction with a kraft mill. In cases where the NSSC mill exists alone, the spent cooking liquor (after evaporation) may be oxidized in a fluidized bed reactor. The product (a mixture of Na_2CO_3 and Na_2SO_4) of this patented process is not suitable for re-use by the NSSC mill and in fact it usually must be enriched with sulfur before it is suitable for use in the kraft process. This is accomplished by adding sulfur to the fluidized bed unit along with the feed liquor.

3.3.1.3 NSSC Fluidized Bed Recovery Process

Figure 3-17 shows the fluidized bed system for treatment of neutral sulfite pulping waste liquors. In these mills, a pulping liquor containing sodium sulfite (Na_2SO_3) and sodium carbonate (Na_2CO_3) is used as the pulping medium. During pulping, lignin and other organic matter is extracted from the wood and the spent pulping liquor contains sodium-sulfur compounds of varied degrees of oxidation in association with the organic matter extracted from the wood. The total solids in the spent pulping liquor have a gross heating value of about 5,500 BTU per pound (dry), contain about 30 percent carbon and 3 percent hydrogen.

The spent pulping liquor is received from the pulp washing operation at about 10 percent total solids. In order to support autogenous combustion of the liquor in a fluidized bed reactor, it is necessary to concentrate the waste liquor to about 35 percent total solids, at which point the fuel values in the waste can sustain combustion without addition of external fuel. This concentration is accomplished in multiple-effect vertical-tube forced-circulation evaporators of a special design to minimize tube fouling. Nominally, a three-body, three-effect evaporation unit is employed at a steam economy of about 2.6. The concentrated liquor, at about 35 percent total solids, is pumped to a storage facility before introduction into the fluidized bed reactor.

The temperature of the fluidized bed reactor is maintained at about 1,325°F. The concentrated liquor is introduced as a liquid dispersion into the freeboard area of the reactor. This method has several advantages over introduction of the liquid feed below the level of the fluidized bed. As the liquid feed contacts the heated exhaust gases rising from the fluidized bed, a portion of the water content of the feed is evaporated and the remainder of the feed falls into

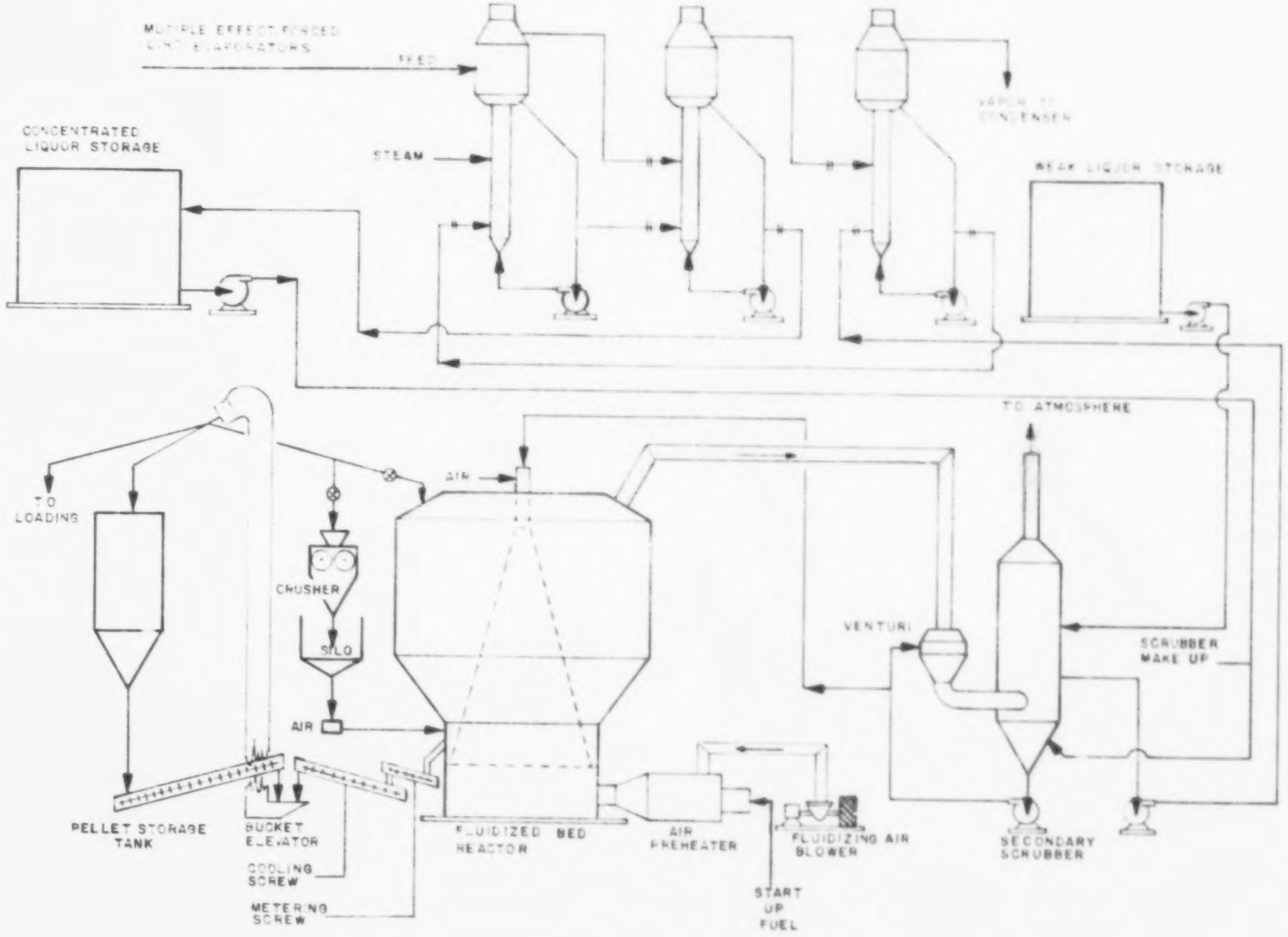

MUTIPLE EFFECT FORCED
CIRC. EVAPORATORS
FEED
STEAM
VAPOR TO
CONDENSER
CONCENTRATED
LIQUOR STORAGE
WEAK LIQUOR STORAGE
TO ATMOSPHERE
AIR
TO
LOADING
CRUSHER
SILO
AIR
VENTURI
SCRUBBER
MAKE UP
PELLET STORAGE
TANK
BUCKET
ELEVATOR
COOLING
SCREW
METERING
SCREW
FLUIDIZED BED
REACTOR
AIR
PREHEATER
FLUIDIZING AIR
BLOWER
START
UP
FUEL
SECONDARY
SCRUBBER

FIGURE 3-17. COPELAND RECOVERY SYSTEM FOR NSSC PULP MILLS

the fluidized bed. In the bed, the organic portion of the feed is oxidized to carbon dioxide and water vapor and the residual inorganic chemicals are oxidized to their stable oxidation state; i.e., sodium sulfate and sodium carbonate. Oxidation of the organic matter provides sufficient thermal energy to maintain the reaction temperature. The product of the inorganic chemicals, sodium sulfate and sodium carbonate, deposits in the bed and forms the bed material. The chemical product can be made to pelletize or agglomerate in the fluidized bed, and the product is discharged as a nearly perfect sphere in the size range of 20 to 65 mesh.

The exhaust gases, containing entrained particulate material, are passed through a cyclone separator where entrained material is separated from the exhaust gases and returned through a screw conveyor or steam ejector directly to the fluidized bed. The exhaust gases are scrubbed with weak waste liquor to remove any remaining entrained particles and to recover a portion of the sensible heat content of the exhaust gases. Analysis of these exhaust gases, for the presence of offensive gaseous compounds, indicates that the effluent contains little if any compounds that might contribute to air pollution. There are no reduced or partially oxidized gaseous sulfur compounds.

3.3.1.4 Direct Sulfitation in Recovery Boilers or Smelters

Another class of NSSC process is that which recovers sulfite cooking liquors directly. The I.P.C. Mead and Western Precipitation processes are typical of this group. The process essentially is a recovery boiler (smelter) modified to produce sodium sulfite rather than sodium sulfide. Some of these are conversions of old kraft recovery boilers, others may be new equipment designed for this service.

3.3.1.4.1 Spent Chemical Recovery Cycle

The black liquor filtrate separated from the softened chips and mechanical pulp is concentrated in multiple effect and/or direct contact evaporators to the desired solids concentration. The concentrated black liquor is sprayed into a furnace, usually with an auxilliary fuel such as oil. The furnace is maintained at 1,000°F to 1,300°F.

In the furnace, the sprayed liquor droplets flash dry. The carbonaceous material chars in the upper oxidizing atmosphere of the furnace and the inorganic carbonate, sulfur salts, and char fall to the bottom of the furnace where a bed forms. Primary air to the bed is controlled to maintain reducing conditions which will convert sulfur-containing salts to sodium sulfide. Secondary air admitted above the bed burns hydrogen sulfide to sulfur dioxide and completes the combustion of the carbonaceous material. The sodium sulfide and sodium carbonate form a molten smelt which flows from the furnace and is dissolved in water to form a solution referred to as "green liquor".

Because of the sulfur compounds in the black liquor the flue gas from the furnace contains some sulfur dioxide, and may contain reduced sulfur compounds. In order to achieve efficient chemical recovery, the sulfur dioxide must be absorbed from the combustion gases with sodium carbonate or caustic solution, a process which presents special problems because of the low sulfur dioxide concentration. Scrubbing can also help to remove hydrogen sulfide and methyl mercaptan.

The flue gases also contain sodium sulfate dust with some sodium carbonate. For efficient chemical recovery, this particulate matter must be removed by electrostatic precipitators or high efficiency venturi scrubbers.

3.3.1.4.2 Preparation of Pulping Chemical

The green liquor, rich in sodium carbonate and sodium sulfide, is pumped to the top of an absorption tower. There the solution is brought in contact with sulfur dioxide from a sulfur burner. The concurrent scrubbing of the SO_2-laden gas by the green liquor results in the following reactions:

$$2Na_2CO_3 + SO_2 + H_2O \rightarrow Na_2SO_3 + 2NaHCO_3$$

$$Na_2S + SO_2 + H_2O \rightarrow Na_2SO_3 + H_2S$$

The scrubbing towers are efficient in their absorption of the sulfur dioxide. There is, however, a large quantity of hydrogen sulfide produced which must be burned to sulfur dioxide and abosrbed in sodium carbonate or eliminated in some other way if atmospheric pollution is to be avoided. The sulfited green liquor emerges from the absorption tower as "cooking liquor" and is ready for reaction with wood chips in the digester.

3.3.2 OTHER NSSC RECOVERY PROCESSES

There are several variations of the NSSC recovery processes based on burning the spent liquor, and three of these will be briefly discussed under this section, and as shown in Figures 3-18 through 3-20.

3.3.2.1 Mead Process

The first of the three methods to be discussed is the Mead Process, developed and patented by The Mead Corporation. Basically, the process operates by separating the sulfur from the sodium complex by carbonation of the green liquor with waste flue gas. The sulfur, driven off as H_2S, can then be oxidized by burning in air either in the furnace or in a special burner, and is then recombined with sodium by washing the SO_2 containing gases with the sodium carbonate solution formed in the first step. Processes similar in general approach have a considerable history, but this process has several novel features which are what make it feasible. The scrubbing of the totality of furnace flue gases with a Na_2CO_3 solution gives a clean, SO_2 free, CO_2 rich, gas to use for carbonation, as well as minimizes sulfur losses. The splitting of the gas stream between the precarbonation and carbonation towers provides the maximum concentration of H_2S to the furnace and still does not result in sulfur loss.

Following through the process, the concentrated liquor from the multiple effect evaporators is evaporated further in the venturi scrubber-evaporator. This liquor is burned in a kraft type furnace, which operates with a reducing atmosphere in the "hearth" zone. The molten Na_2S - Na_2CO_3 mixture flows into a dissolving tank. The green liquor is then clarified.

The flue gases from the furance pass through the superheater, boiler and economizer for purposes of steam production, and then to the venturi scrubber where the gas velocity is increased and black liquor is injected into the gas stream. The high gas velocity (approximately 300 fps) atomizes the liquor. This provides a cloud of droplets with a tremendous surface for heat transfer and on which the dust in the flue gas is collected. The liquor is spearated from the flue gas in the cyclone separator, and the clean gas containing N_2, CO_2, O_2 and SO_2 is passed to the sulfiting tower.

The sulfiting tower makes the cooking liquor by absorption of the SO_2 from the flue gas in a Na_2CO_3 solution. This carbonate solution is obtained from the carbonating towers, where it is made by carbonation of green liquor with a part of the clean, substantially SO_2 free, flue gas from the sulfiting tower. It is in these carbonation towers that the sulfide in the green liquor is removed as H_2S.

The gases leaving the carbonating tower contain H_2S and the CO_2 not used in carbonization. The concentration of this H_2S is sufficiently low to present difficulty in combustion. Therefore, the precarbonation tower is a device used to bring about an increase in H_2S concentration. About a third of the gas leaving is passed through this tower. The high alkalinity of the liquor at this point removes the H_2S from the gas stream, forming NaHS. The gases leaving this tower can be discarded with

FIGURE 3-18. MEAD PROCESS SIMPLIFIED FLOW SHEET

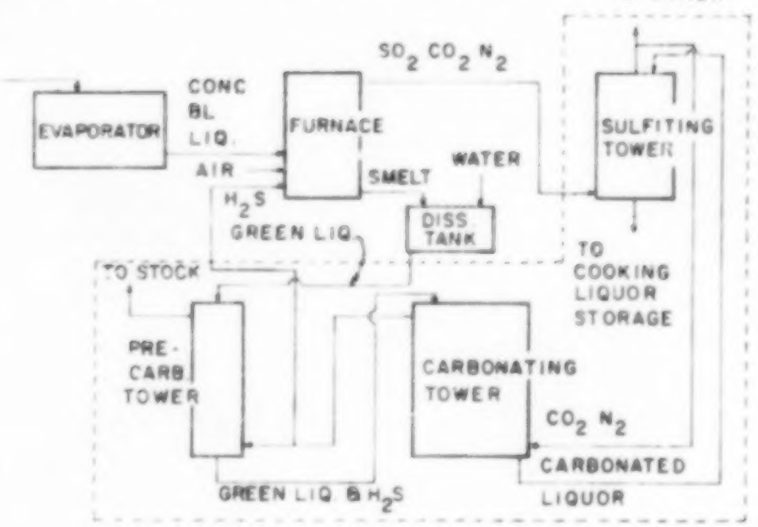

TO STACK
SO_2 CO_2 N_2
EVAPORATOR
CONC
BL
LIQ.
AIR
FURNACE
SMELT
WATER
SULFITING
TOWER
H_2S
GREEN LIQ.
DISS.
TANK
TO STOCK
TO
COOKING
LIQUOR
STORAGE
PRE-
CARB.
TOWER
CARBONATING
TOWER
CO_2 N_2
CARBONATED
LIQUOR
GREEN LIQ. & H_2S

FIGURE 3-19. INSTITUTE PROCESS SIMPLIFIED FLOW SHEET

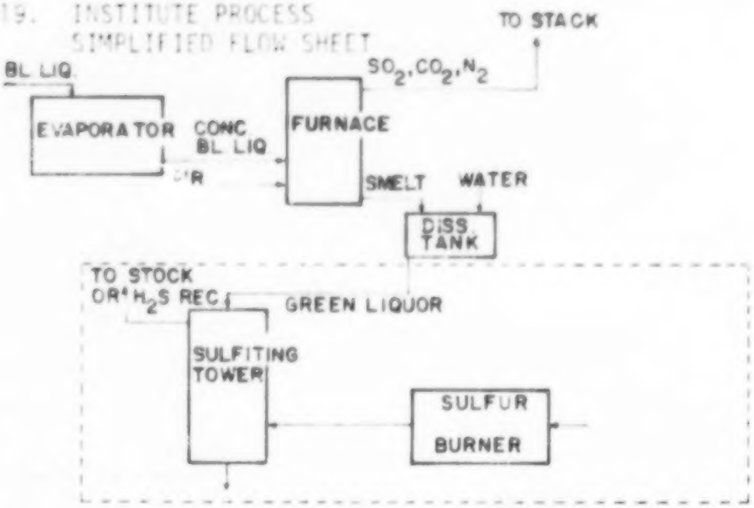
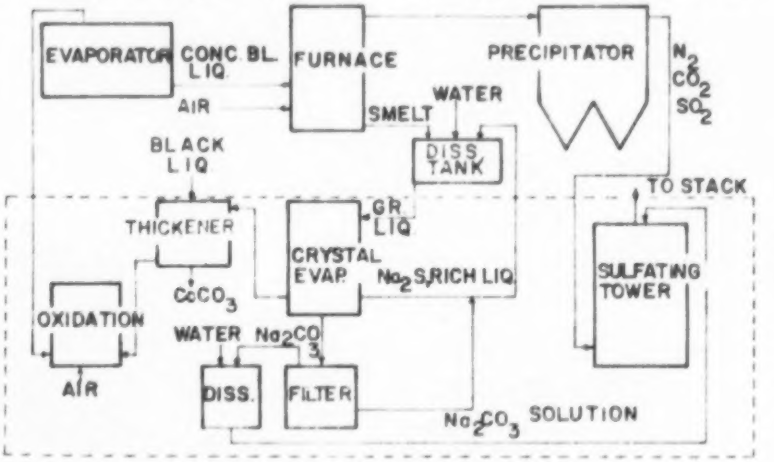

TO STACK
BL. LIQ.
SO_2, CO_2, N_2
EVAPORATOR
CONC.
BL. LIQ.
AIR
FURNACE
SMELT
WATER
DISS.
TANK
TO STOCK
OR H_2S REC.
GREEN LIQUOR
SULFITING
TOWER
SULFUR
BURNER

FIGURE 3-20. WESTERN PRECIPITATION PROCESS SIMPLIFIED FLOW SHEET


EVAPORATOR
CONC. BL.
LIQ.
AIR
FURNACE
PRECIPITATOR
N_2
CO_2
SO_2
SMELT
WATER
DISS.
TANK
BLACK
LIQ.
TO STACK
THICKENER
GR.
LIQ.
CRYSTAL
EVAP.
Na_2S RICH LIQ.
SULFATING
TOWER
$CaCO_3$
OXIDATION
WATER
Na_2CO_3
AIR
DISS.
FILTER
Na_2CO_3 SOLUTION

negligible loss in sulfur, while the H S thus absorbed will be released in the carbonation tower. Consequently, there is a very substantial enrichment in H S content of that portion of the gases returned to the furnace, insuring satisfactory combustion.

3.3.2.2 I.P.C. Process

The next process to be discussed is one involving direct sulfitation of the green liquor (Figure 3-19). This process has been developed by the Institute of Paper Chemistry. It is a less complex system in that no sulfur recovery is attempted. The drawback to the process lies in the production of some Na S O which, although inert in the NSSC cook, results in higher overall chemical losses and possible difficulties with bleaching. The sulfur losses are complete unless the H S formed is recovered.

3.3.2.3 Western Precipitation Process

Basically, the process uses the furnace as a carbonator and, by increasing green liquor concentration, Na CO is salted out. The sulfide rich mother liquor is recycled to the multiple effect evaporators and added to the entering black liquor. The sulfide is stabilized by oxidation to prevent losses through evolution of H S during evaporation and subsequent venting. A simplified flow sheet based on the published information is shown in Figure 3-20. By scrubbing the flue gases from the recovery unit with the carbonate solution, this process could achieve high recovery efficiencies. It is no simpler than the other processes, with its oxidation and crystallization replacing gas absorption and stripping, but it has some advantages. One simplification is that no H S has to be piped from a tower to a burner.

3.3.3 EMISSIONS FROM NSSC PULPING

Because of the milder pulping conditions employed, the emissions from semichemical plants are less intense than those from conventional pulping processes. The emissions will also vary depending on the process employed; e.g., neutral sulfite, or kraft. In the latter case, the air pollution problems will parallel those described under kraft pulping but will be of a lower order of magnitude. Particulate problems from recovery furnaces are much the same throughout the industry.

Published data on emissions from NSSC pulping are virtually nonexistent. Certainly information exists in the files of various mill engineering departments and perhaps in the files of state and local control agencies. This data is proprietary however and not available. The data in Table 3-5 have been excerpted from various technical and commercial publications. The data for newer technology represent improvements made in

TABLE 3-5

EMISSIONS FROM NSSC PULPING (LBS/TON ADP)

Source	Pollutant	Old Technology	Newer Technology
Recovery Furnace or Smelter	SO_2	8.20	2.45 - 1.40
	H_2S	4.20	1.10 - 0.20
	RSH	0.30	0.10 - 0.05
	Total	12.70	3.65 - 1.65
Sulfiting Tower	SO_2	0.80	0.30
	H_2S	8.55	-
	Total	9.35	0.30
Blow Tank	SO_2	0.30	0.25
	H_2S	4.20	2.10
	RSH	1.56	0.78
	Other Organic	3.12	1.50
	Total	9.18	4.63
Dissolving Tank	H_2S	0.10	0.10
	SO_2	0.04	0.04
	Total	0.14	0.14
Evaporator	H_2S	0.13	0.13
	Total Organic S	0.09	0.09
	Total	0.22	0.22
Washers	H_2S	0.05	0.05
	SO_2	0.01	0.01
	Total	0.06	0.06
Fluidized Bed	SO_2		.004 - .008
	Total Organic S		.004 - .007
	Total		.008 - .015
Copeland Process	SO		0.06 - 0.20
	Total Organic S		0.18 - 0.32
	Total		0.24 - 0.52

the past five to six years. Combination of NSSC spent liquor with kraft black liquor prior to evaporation and combustion results in an increased sulfur dioxide and hydrogen sulfide emission from the kraft recovery system. No quantitative data on this increased emission rate are available.

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3.3.4 THE EFFECT OF PROCESS AND CONTROL EQUIPMENT VARIABLES ON PULP PRODUCTION AND EMISSIONS

The following sections describe variables in process and emission control which affect pulp production rates and attendant emission levels for the NSSC pulping process.

3.3.4.1 Liquor Pyrolysis and Chemical Recovery Operations

Many of the unit operations utilized in both the NSSC and sulfite processes are similar to those used in kraft operations. Therefore, the variable relationships and their subsequent effect on emissions would be similar, although the range magnitude may differ somewhat.

NSSC spent liquors are treated in a number of ways, and there exists very little information regarding process variable and control equipment effects on the attendant emissions. The various methods for recovery have been previously discussed in this chapter, which included among other kraft-NSSC cross-recovery, fluidized bed, and a modified "kraft type" recovery boiler. Kraft-NSSC cross-recovery has been discussed under kraft recovery boiler operations and therefore will not be further discussed.

3.3.4.2 Chemical Recovery Furnace

There is a relationship between the Na/S ratio in the liquor and the emission of sulfur dioxide. When TRS emissions are reduced the Na/S ratio decreases and sulfidity increases. Consequently, less alkali is available for recombination with the SO_2 in the secondary zone and thus SO_2 emission increases. Figure 3-21 gives the experimental data showing the relationship between Na/S ratio and SO_2 emissions.

Adequate turbulence and cooling of the gases is essential to promote efficient recombination and low alkali losses. There is a need of about a 1000°F drop in temperature for best recombination results, but it should be rapid to avoid formation of other sulfur compounds. Cool tertiary air is also considered to be helpful.

3.3.4.3 Sulfitation Towers

Sulfur dioxide from sulfur burners or other make-up sources are scrubbed with an alkaline solution of sodium base in the amount required by the Na make-up of the mill. The solution should have a molar ratio bisulfite/sulfite of 4:1 at a pH of around 7.0.

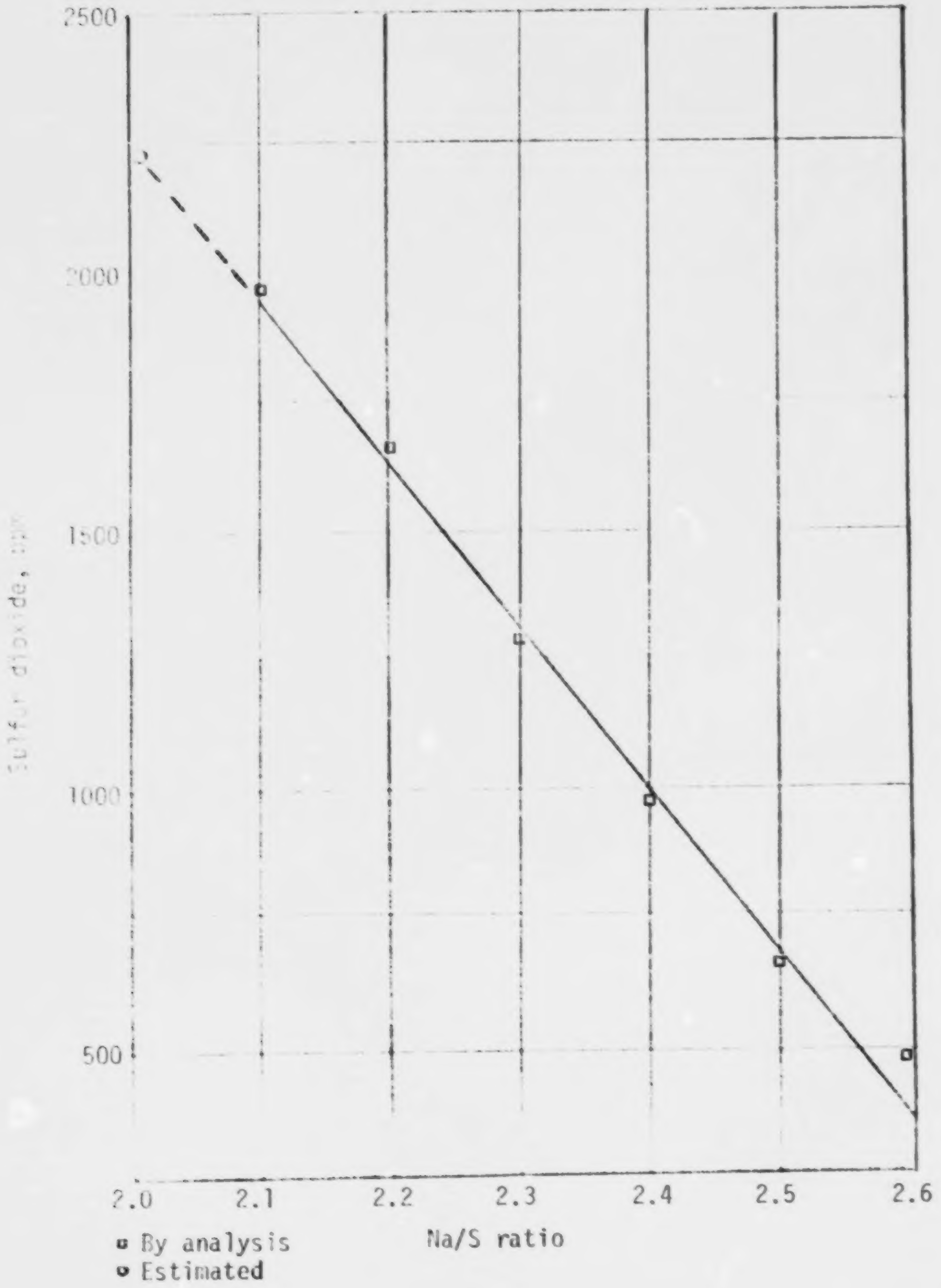


FIGURE 3-21

SULFUR DIOXIDE REDUCTION WITH INCREASE IN Na/S RATIO

The formation of the bisulfite-sulfite solution takes place in the original sulfitation tower. The bisulfite-sulfite liquor can be contacted with green liquor instead of directly with the smelt, as is often done.

3.3.4.4 Direct Contact Evaporation

In this type recovery operation, where direct contact evaporators are involved, removal of SO_2 is an important tool in reducing the total emission of sulfur from the smelter, since the smelter, per se, does not favor the best control of sulfide and sulfur oxide emissions. In order to improve emission control from the smelters, existing concentrated black liquor used in the venturi evaporators may be replaced with a weaker black liquor, containing 12-17 percent solids for instance.

3.3.4.5 Fluidizied Bed Pyrolysis Operations

Emissions associated with the operation of fluidized bed units were previously discussed. These systems are not nearly so complex as other recovery methods; and, based on the limited data available, indications are that emissions for these sources are minor.

The major variables associated with fluidized bed operations, which could affect emissions, are the feed solids concentration, combustion bed temperature, fluid bed height, and the feed liquor sodium/sulfur ratio. The main variables affecting the venturi evaporator-scrubber performance are pressure drop across the scrubber and scrubbing liquor solids concentration.

3.4 DESCRIPTION OF SULFITE PROCESS

The sulfite pulping process produces easy bleaching pulps from non-resinous woods. The characteristics of the pulp make it suitable for use in many grades of paper, but it is especially suitable for tissues and fine papers.

Recovery of cooking chemicals and the heat values in the spent cooking liquors was not widespread until fairly recent years when the older calcium base has been replaced in many mills by a soluble base such as sodium, magnesium, or ammonium. Sodium and magnesium bases require recovery for economic reasons. Of the two, magnesium is more widespread in its use because on combustion the inorganic constituents break down directly to magnesium oxide and sulfur dioxide which can readily be recycled.

Spent liquors from ammonia base pulping may be incinerated with recovery of most of the SO_2. The ammonia burns completely to nitrogen and water vapor.

3.4.1 GENERAL DESCRIPTION OF SULFITE PROCESS

Sulfite pulping is an acid chemical method of dissolving the lignin that bonds the cellulose fibers together. Many of the older mills use a sulfurous acid - calcium bisulfite solution for the cooking acid. Calcium-base spent liquor, because of problems associated with evaporation and chemical recovery, is discarded and may result in water pollution problems. In order to overcome the problem of water pollution, several other acid bases have been developed, the most important being sodium, magnesium, and ammonium.

Because sulfite pulp is used in a wide variety of end products, operations will vary considerably between mills. These products can include pulp for making high grade book and bond papers or tissues for combining with other pulps, and for making dissolving pulp for producing cellophane, rayon, acetate, films, and others.

The pulping operation involves cooking the wood chips in the presence of an acid within a digester. The heat required for cooking is produced by the direct addition of steam to the digester or by the steam heating of the recirculated acid in an external heat exchanger. The cooking liquor, or acid, is made up of sulfurous acid and a bisulfite of one of the four above mentioned bases. The sulfurous acid is usually produced by burning sulfur or pyrites and absorbing the SO_2 in liquor. Normally, part of the sulfurous acid is converted to the base bisulfite to buffer the cooking action. During the cooking action, it is necessary to vent the digester occasionally as the pressure rises within the digester. These vent gases contain large quantities of sulfur dioxide and, therefore, are recovered for reuse in the cooking acid.

Upon completion of the cooking cycle the contents of the digester, consisting of cooked chips and spent liquor, are discharged into a tank. During this operation some water vapor and fumes escape to the atmosphere from the tank vent. The pulp then goes through a washing stage, where the spent liquor is separated from the fibers. The washed pulp is either shipped or kept within the plant for further processing. Block diagram flowsheets of the sulfite pulping processes are contained in Figure 3-22.

The spent liquor that was washed out of the pulp can be discarded or, as an alternative, can be concentrated by evaporation and run through a recovery cycle. The concentrated liquor is sprayed into a furnace where the organic compounds are burned. The residual inorganic compounds may be collected and reused in the manufacture of cooking acid.

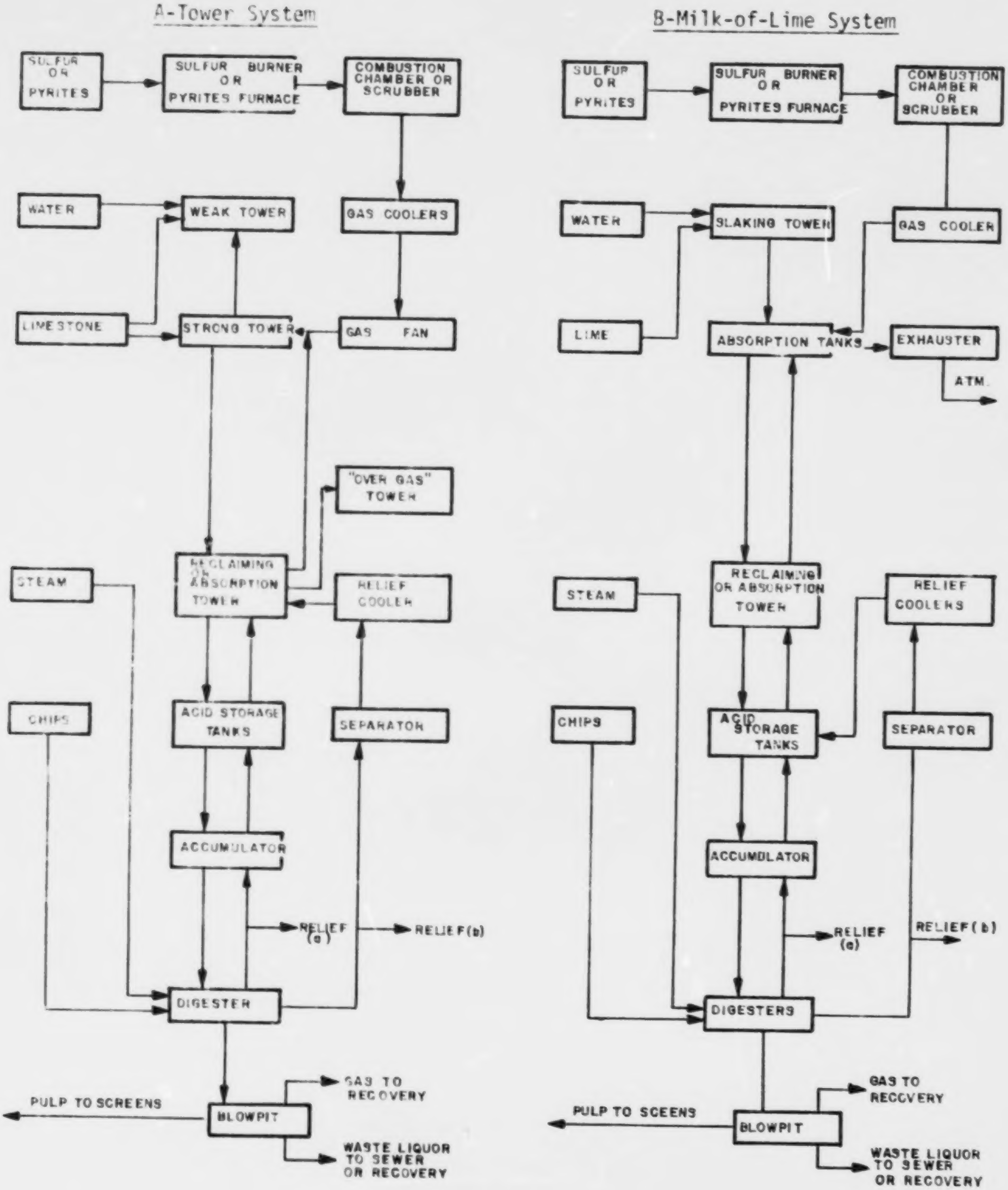

A-Tower System
SULFUR OR PYRITES
SULFUR BURNER OR PYRITES FURNACE
COMBUSTION CHAMBER OR SCRUBBER
WATER
WEAK TOWER
GAS COOLERS
LIMESTONE
STRONG TOWER
GAS FAN
"OVER GAS" TOWER
STEAM
RECLAIMING OR ABSORPTION TOWER
RELIEF COOLER
CHIPS
ACID STORAGE TANKS
SEPARATOR
ACCUMULATOR
RELIEF (a)
RELIEF (b)
DIGESTER
GAS TO RECOVERY
PULP TO SCREENS
BLOWPIT
WASTE LIQUOR TO SEWER OR RECOVERY
B-Milk-of-Lime System
SULFUR OR PYRITES
SULFUR BURNER OR PYRITES FURNACE
COMBUSTION CHAMBER OR SCRUBBER
WATER
SLAKING TOWER
GAS COOLER
LIME
ABSORPTION TANKS
EXHAUSTER
ATM.
STEAM
RECLAIMING OR ABSORPTION TOWER
RELIEF COOLERS
CHIPS
ACID STORAGE TANKS
SEPARATOR
ACCUMULATOR
RELIEF (a)
RELIEF (b)
DIGESTERS
GAS TO RECOVERY
PULP TO SCEENS
BLOWPIT
WASTE LIQUOR TO SEWER OR RECOVERY

FIGURE 3-22. SULFITE PULPING FLOW SHEETS
DIRECT OR INDIRECT COOKING
WITH OR WITHOUT FORCED LIQUOR CIRCULATION

3.4.2 SULFITE PROCESS VARIATIONS

There are a wide variety of processes in use for recovery and disposal of spent sulfite pulping liquors. Because for a number of years there was little attempt to recover chemicals at all, and during the ensuing years a variety of systems were applied as process modifications, there is very little available comparing operating variables. Only recently have several systems been designed for complete recovery applications in sulfite operations. This section will be devoted to briefly discussing some of the operating variables associated with certain systems.

3.4.2.1 Ammonia-Base Liquor Burning and Sulfur Dioxide Recovery

The use of ammonia-base for sulfite pulping requires consideration of waste liquor burning and recovery of sulfur dioxide - the combustion product. Depending on the pulp products desired, an ammonia-base mill can use any one of three basic pulping techniques: acid sulfite, bisulfite, and neutral sulfite semichemical.

Coupled with the liquor burning process, one of the combustion products, sulfur dioxide reacts in an absorption system with anhydrous or aqueous ammonia makeup chemical to produce ammonium bisulfite acid. Several mills in North America are burning ammonia--base liquor without sulfur dioxide recovery.

Limited data from the test on ammonia-base liquor burning indicates solid loading in the stack gases was 1 lb per 1000 lb of flue gas under stable operating conditions. Limited flue gas analyses showed 1% sulfur dioxide by volume on a dry basis and 100 to 300 ppm of sulfur trioxide. It has been determined small variations in firing liquor solids content can have a major influence on the heat load and burning intensity. The higher flame temperature should reduce unburned carbon carry over.

Burning intensity is also adversely affected by large particle size, hence the necessity to obtain good atomization. Good atomization is affected by liquid viscosity. Table 3-6 and Figures 3-23 and 3-24 relate some of the operating variables associated with ammonia-base liquor burning.

In absorption system design, interdependent factors affecting absorption effectiveness must be balanced. Acid concentration, concentration of sulfur dioxide in the gas, and operating temperature determine the arrangement and amount of absorption surface.

Table 3-6. Ammonia-Base Liquor Burning Tests.

	Test 1	Test 2	Test 3	Test 4
Liquor rate, lbs/hr	773	909	1100	815
Solids concentration, %	48.4	44.6	53.7	54.6
Natural gas rate, lbs/hr	180	157	0	0
Heat release rate, million BTU/hr	6.9	6.7	5.1	3.75
Total air at stack, %	105	108	110	114
Air temperature, °F	500	750	750	550
Liquor temperature, °F	206	165	165	165
Furnace exit gas temperature, °F	2240	1800	1820	1750
Stack dust loading, lbs/1000 lbs gas	---	0.70	1.4	0.70
Average SO_2 at stack volume, %	0.42	0.9	1.13	1.01
Average SO_3 at stack volume, ppm	70	84	350	10

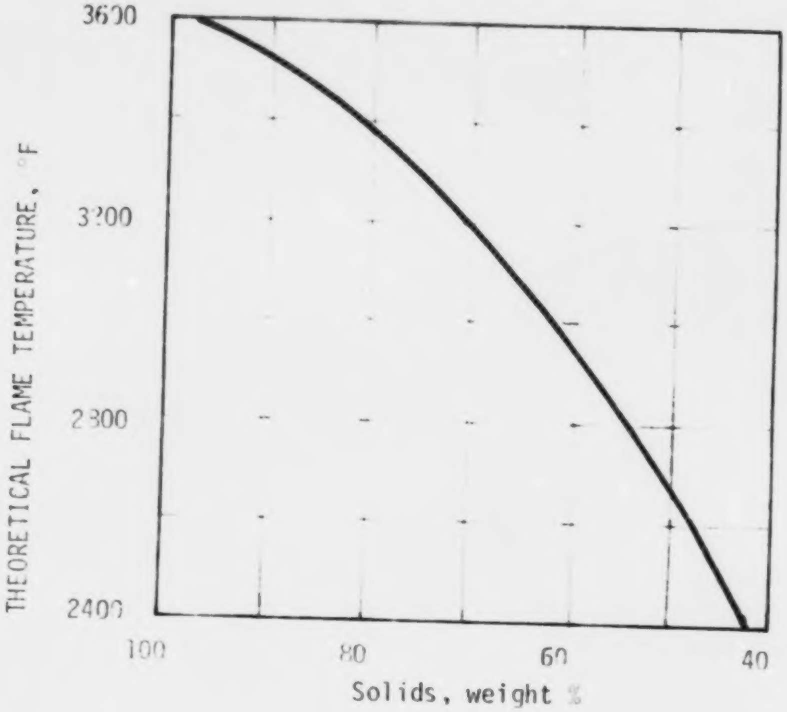


Figure 3-23. Effect of ammonia-base liquor solids content on flame temperature.

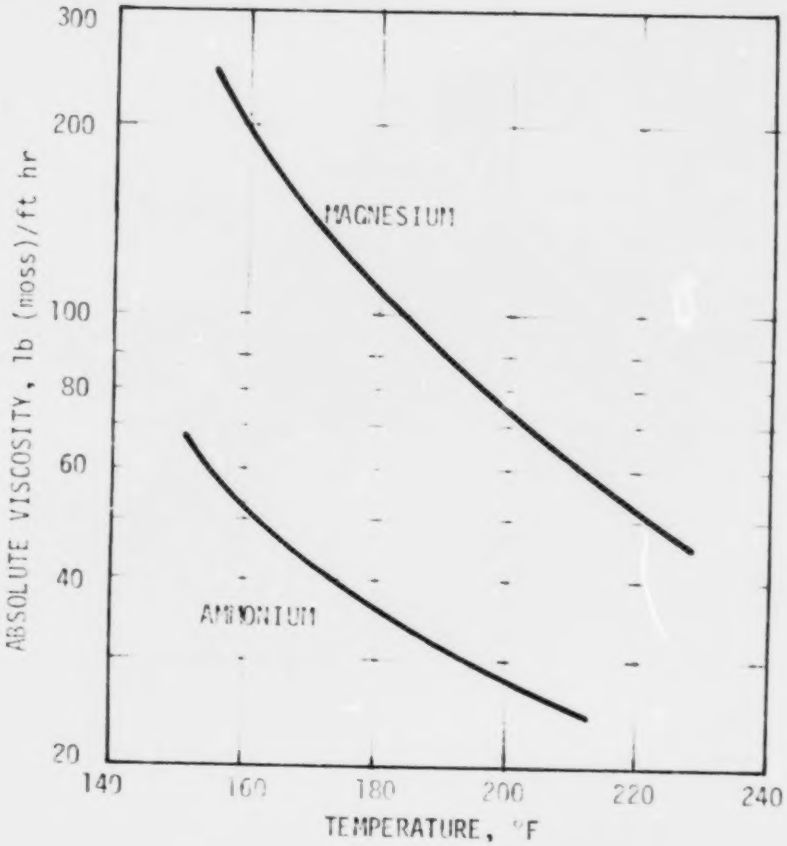


Figure 3-24. Viscosity of ammonia and magnesium liquors (54.5% solids content.)

Available technology limits absorption system design to a temperature level of about 100°F, requiring that the combustion gases leaving the boiler be cooled by dehumidification before entering the absorption equipment. In one operation, combustion gases were cooled to 104° in a packed cooling tower, and 99% recovery of sulfur was achieved from gases containing 0.5-0.7 vol. % sulfur dioxide in the production of a 6.25 pH solution of ammonium bisulfite and sulfite.

3.4.2.2 Magnesium Oxide Recovery System

The recovery of magnesium in a sample recovery system is made possible by the chemical and physical properties of the base chemical. Spent liquor burned at elevated temperature in a controlled oxidizing atmosphere yields the base in the reusable form of an active magnesium oxide. The oxide is readily recombined in a simple secondary system with sulfur dioxide produced in the combustion to yield cooking acid for pulping.

The concentration of sulfur dioxide in the stack gas from a recovery system can be maintained at less than 250 ppm by dry volume. For a magnefite mill, this is about 3 lbs sulfur per ton of unbleached pulp, which is a small amount compared to the total mill sulfur loss of 70-80 lbs/ton. The 250 ppm is equivalent to 2-3% of the sulfur in the liquor feed to the recovery furnace.

The sulfur dioxide recovery efficiency of the three absorption venturis has been measured at 97.5% when producing an acid with an average concentration of 5.7% total sulfur and 3.2% combined sulfur dioxide. Concentrations of sulfur dioxide in the gases entering and leaving each absorption venturi are plotted in Figure 3-25. There is considerable difference in the capacity and performance of recovery systems designed for the various processes. This diversity is presented by Tables 3-7 and 3-8, using as a basis of comparison typical conditions for a kraft recovery unit.

3.4.2.3 Other Magnesium Oxide Sources

Test data from a magnefite pulp recovery system presented by Figure 3-26 illustrates factors to be considered in an evaluation of secondary system performance. The system consists of a packed tower for cooling combustion gases to 104°F prior to their entering a series of three absorption venturis.

Sulfur dioxide gas from the burning of makeup sulfur enters the recovery system at the induced draft fan inlet after passing through the fortification system and this quantity is included in the gas analysis at the cooling tower inlet. Digester relief gases enter the recovery system at the base of the cooking tower.

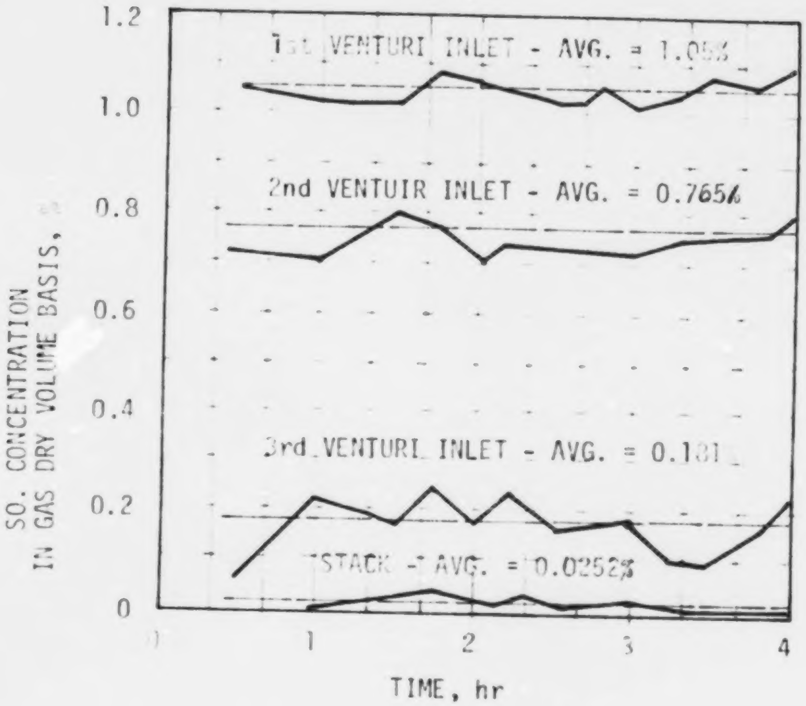


Figure 3-25. Secondary recovery system performance for a product acid composed of 5.75% total SO_2 and 3.25% combined SO_2.

Table 3-7. Recovery Unit Performance - Relative Comparison for 1-lb Solids.

	Board Linerboard	Magnefite News Furnish	Magnesium and Bisulfite Dissolving Grade
Liquor heating value, BTU/lbs solids	6600	6800	8000
Thermal efficiency, % total input	59.7	64.1	68.9
Steam generation, lb/lb solids	3.7	4.1	5.2
Flue gas leaving evaporator, lb/lb solids	7.0	7.0	8.5

Table 3-8. Recovery Unit Performance at 300 Tons/Day Air-dried Unbleached Pulp

	Linerboard	Magnefite News Furnish	Magnesium and Bisulfite Dissolving Grade
Lb solids/a.d. ton unbleached pulp	3000	1850	3200
Yield, % (approximate)	45	60	37
Solids flow, lb solids/hr	37,500	23,120	40,000
Total heat input, million BTU/hr	213	169.5	343.0
Steam flow, lbs/hr	139,000	95,000	208,000
Lb steam, ton pulp	11,120	7,600	16,649
Flue gas leaving cyclone evaporator, lbs/hr	262,500	162,000	340,000

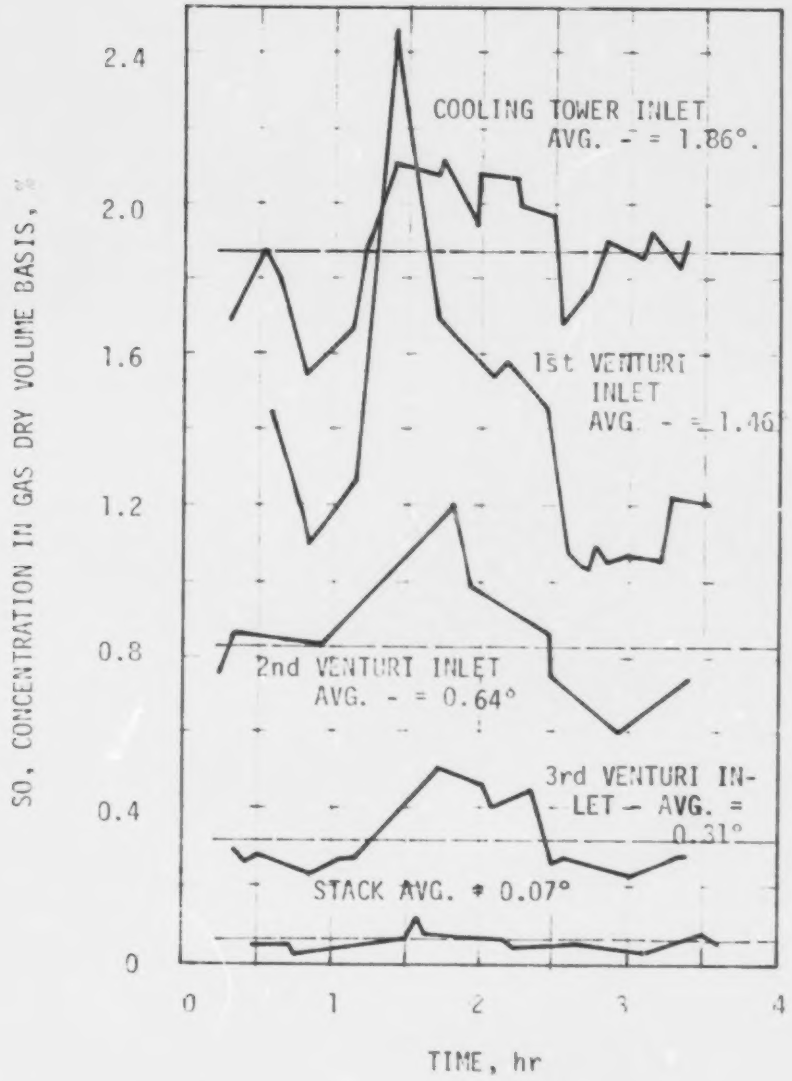


Figure 3-26. Secondary recovery system performance for a product acid composed of 6.1% total SO_2 and 3.2% combined SO_2.

Overall performance data indicates that the concentration of sulfur dioxide in the gas discharged to the atmosphere gives a more definite measure of system performance than an efficiency value based on inlet and outlet concentrations of sulfur dioxide.

3.4.2.4 Jenssen Exhaust Scrubber

Sulfite cooking acid is often produced in a Jenssen-type, two tower limestone system. Data show that weak tower exhaust contains an average of 0.5% SO_2 with trace amounts of sulfur trioxide. These data are summarized in Table 3-9. Typical mass transfer type scrubbers have resulted in SO_2 recovery efficiencies of over 98%, with about 50 ppm SO_2 in the scrubber exit gases. Data on the liquid composition of the $NaOH-SO_2-H_2O$ system as a function of pH are plotted in Figure 3-27, and a schematic of the scrubbing system indicating controlled variables is shown in Figure 3-28.

3.4.2.5 Scrubbing Blowpit Gases

Sulfur dioxide loss from digester blowpit vents is a major emission source for most sulfite pulp mills. Such losses may be virtually eliminated by the application of a chemical scrubber on the residual gas from an existing water absorption SO_2 recovery system. The gas collection system for the scrubber is designed such that a portion of the high volume, low SO_2 content gas released during the initial 45 seconds of the digester blow bypasses the tower and is vented to the atmosphere. During the remaining 13 to 14 minutes of the blow, outside air is drawn in, allowing the scrubber to process a constant volume.

Scrubbing liquor is a mixture of makeup NaOH and a 4.5% solution of $Na_2CO_3/NaHCO_3$ from the recovery process at a pH of 9-10. Operating the tower at a rate of 10,500 lbs/ft^2 liquor and 2,000 lbs/ft^2 gas (90°F) has resulted in SO_2 absorption efficiencies of 99 to 99.5%.

Because nearly all of the sulfite mills built in the past 20 years have used the magnesium-base system, this report will give greater emphasis to a description of that process. The magnesium-base system provides maximum recovery of process chemicals and minimizes air and water pollution problems connected with the pulping system. Aside from the liquor recovery system, however, the sulfite process is independent of the base chemical used. Figure 3-29 illustrates a typical system.

Table 3-9. Jenssen Tower Gas Analysis.

Gas	Concentration Inlet (%)	Concentration Exhaust (%)
Sulfur Dioxide	20.5	0.5
Oxygen	5.1	5.3
Nitrogen	74.3	85.3
Carbon Dioxide	0.1	8.9
Sulfur Trioxide	0.03	0.03

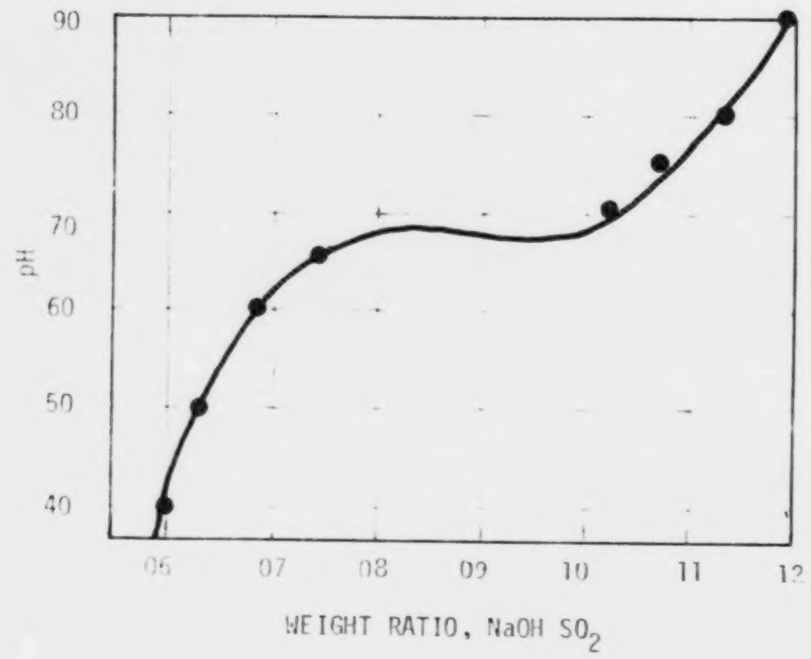


Figure 3-27. Liquid composition of the NaOH SO$_2$-H$_2$O system as a function of pH. By defining two variables, the third is fixed.

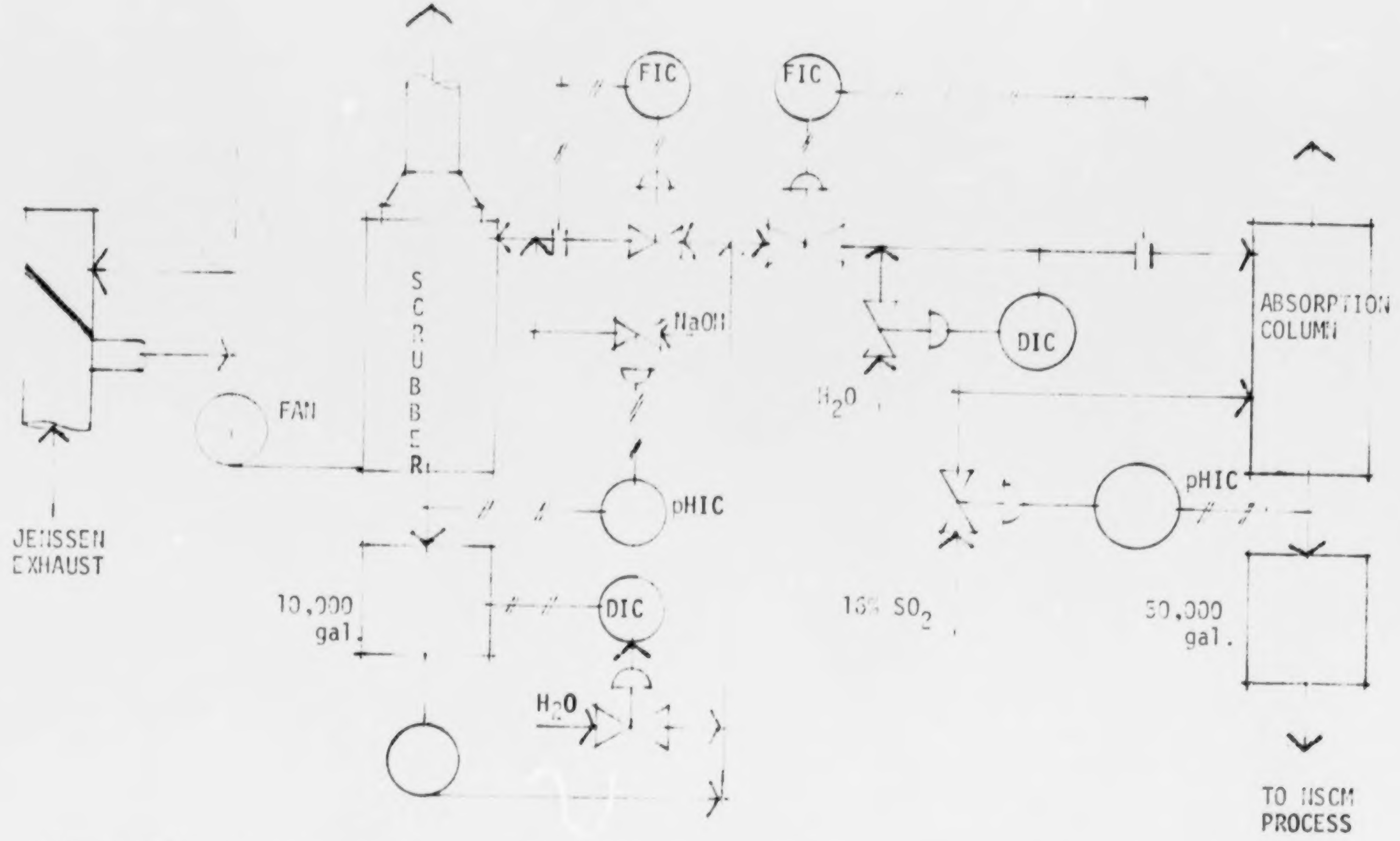

FIC
FIC
S C R U B B E R
NaOH
DIC
ABSORPTION COLUMN
H_2O
FAN
pHIC
pHIC
JENSSEN EXHAUST
10,000 gal.
DIC
16% SO_2
50,000 gal.
H_2O
TO NSCM PROCESS

Figure 3-28. Jenssen exhaust scrubber process flow. (FIC, flow control; DIC, density control; pHIC, pH control.)

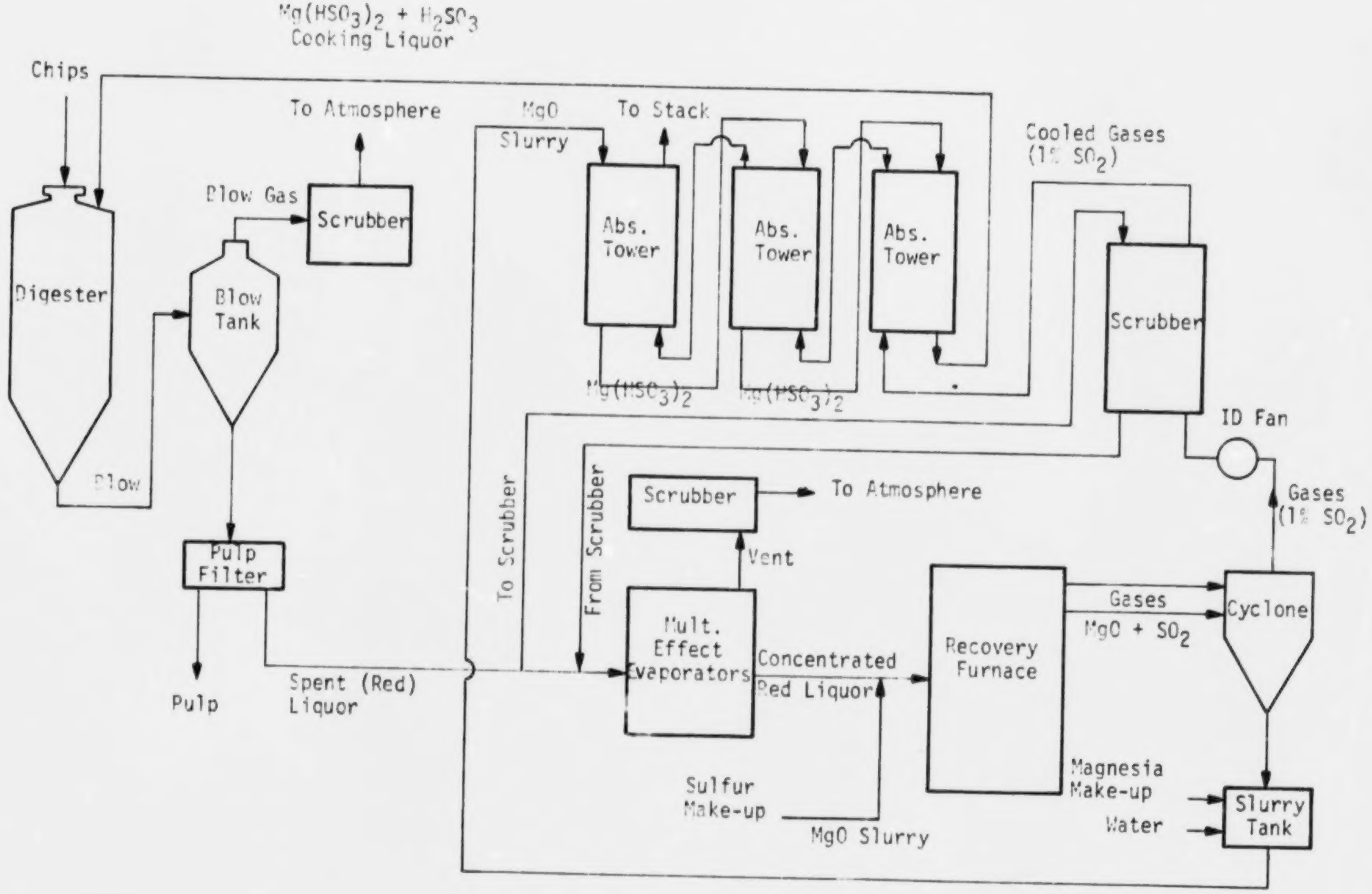

$Mg(HSO_3)_2 + H_2SO_3$
Cooking Liquor
Chips
Digester
Blow
Blow Tank
Blow Gas
Scrubber
To Atmosphere
Pulp Filter
Pulp
Spent (Red) Liquor
MgO Slurry
To Stack
Abs. Tower
Abs. Tower
Abs. Tower
$Mg(HSO_3)_2$
$Mg(HSO_3)_2$
Cooled Gases ($1\% SO_2$)
Scrubber
ID Fan
Gases ($1\% SO_2$)
To Scrubber
From Scrubber
Scrubber
To Atmosphere
Vent
Mult. Effect Evaporators
Concentrated Red Liquor
Recovery Furnace
Gases
$MgO + SO_2$
Cyclone
Sulfur Make-up
MgO Slurry
Magnesia Make-up
Water
Slurry Tank

FIGURE 3-29. SULFITE PULPING PROCESS MAGNESIUM BASE RECOVERY

The cyclone collection system, coupled with the wet scrubbers and absorbers used to remove SO_2 from the recovery furnace gases, control particulate losses from this operation. In addition, many mills generate their own steam and power, and those using fossil fuel and bark are subject to the normal emissions from this type of equipment.

A summary of emission data relative to various sulfite pulping processes is contained in Table 3-10.

TABLE 3-10

SUMMARY OF EMISSION DATA - SULFITE PROCESS
(Emissions in lbs/ADT)

	SO_2	Particulate
Digester Blow Pit	40-100	---
or Dump Tank	10-25	---
Water Scrubbers Following Blow Pit	0.8-20	---
Chemical Scrubbers Following Water Scrubbers	0.015-0.4	---
Jenssen Tower Exhaust	10-15	---
Scrubbers Following Jenssen Tower Exhaust	0.22-0.5	---
Multiple- Effect Evaporators	5-10	---
Recovery Furnaces,(Magnesium Sulfite Process)	50-75	---
Following Scrubbers	3-15	---
Incinerators, Ammonium Base	250-500	---

3.4.3 PULPING PROCESS

The pulping operation (or cook) is carried out in a pressure vessel called a digester. Up to the present time, batch digesters have been used exclusively for sulfite pulping. Recently, the first continuous sulfite digesters have been put into operation. Batch digesters may be as large as 10,000 cubic feet capacity and hold up to 100 tons of wood chips. The cooking liquor, containing a mixture of magnesium bisulfite and sulfurous acid, is pumped into the digester cold and then heated by steam in an external heat exchanger or by direct addition of steam to the digester. Normal maximum cooking temperatures will range from 250°F. to 300°F. at pressures up to 110 psi depending on the pulp grade being made. Cooking times will vary from as low as six hours to as high as 20 hours. Low temperatures and longer cooking times are associated with a special type of sulfite pulp known as Mitscherlich pulp for glassine paper. Where dissolving pulps are being made, careful control at the digesters is extremely important to final pulp quality.

During the cooking cycle, it is necessary to vent the digester occasionally as the temperature rises. These "relief" gases are rich in sulfur dioxide and are collected in accumulators for direct reuse. When the accumulators are operating properly, little or no air pollution is associated with the cooking cycle.

Upon completion of the cooking cycle, the digester pressure is reduced to atmospheric pressure and the pulp is washed into a tank. In some cases, the dump tank has a perforated, false bottom to allow the pulp to be washed in the same tank or blow pit. Newer systems dilute the pulp and pump it to countercurrent drum washers. During the blow, sulfur dioxide and volatile materials are released. The blow gases are normally passed through an absorption tower to remove sulfur dioxide. Although the noncondensable gases from a sulfite mill have a characteristic odor, in general, they have not been considered offensive and in comparison with the much more serious problems associated with kraft pulping, little attention has been paid to the air pollution aspects of sulfite pulping.

After being discharged from the digester, the pulp goes through a washing stage. Spent liquor from this stage is sent to evaporators, if chemical recovery is practiced, and the washed pulp is either sent to the bleach plant or is used directly in products requiring unbleached pulp.

Up to this point in the system, the process is independent of the base used.

3.4.4 SPENT CHEMICAL RECOVERY CYCLE (MAGNESIUM-BASE SYSTEM)

The spent liquor (red liquor) separated from magnesium-base pulp is concentrated in multiple-effect evaporators to the desired concentration for firing the recovery furnace. As the strong red liquor is showered into the furnace, the organics dissolved from the wood burn away, leaving a magnesium sulfite ash. At the temperature of the furnace (about 1600°F.), the ash dissociates into magnesium oxide (MgO) and sulfur dioxide (SO_2). The magnesium oxide is removed from the flue gas by a cyclonic collection system and is slurried in water. This slurry is later caused to react with sulfur dioxide to form the magnesium bisulfite for the cooking acid. The sulfur dioxide is scrubbed from the flue gases with water to form the sulfurous-acid solution for cooking acid.

Chemical recovery is efficient for both magnesium oxide and sulfur dioxide. The wet scrubbers used to recover sulfur dioxide from the flue gases also remove particulate matter getting past the cyclonic separators. The major components of a magnesium bisulfite recovery system are illustrated in Figure 3-30.

3.4.5 PREPARATION OF PULPING CHEMICALS

The magnesium-oxide slurry from the recovery furnace is fed into an absorption tower with sulfur dioxide scrubbed from the flue gases or produced in a sulfur burner. Magnesium bisulfite is formed as follows:

$$MgO + 2SO_2 + H_2O \rightarrow Mg(HSO_3)_2$$

In the preparation of calcium-base sulfite liquor, SO_2 from a sulfur burner is passed through a limestone-packed tower countercurrent with water to form $Ca(HSO_3)_2$. An excess of SO_2 is added to form sulfurous acid according to the need for the grade of pulp being made. Pulp characteristics and pulping conditions can be affected drastically by varying the ratio of "combined" and "free" SO_2. Some minor SO_2 losses may occur around the absorption system, but no data are available with regard to the extent of such losses.

3.5 SULFITE RECOVERY SYSTEMS, PRESENT AND FUTURE PROSPECTS

The choice of a recovery process for sulfite pulping is not a simple one. This is in part because sulfite recovery technology is still in a state of active development, as evidenced by the variety of processes now in use or proposed for use. This is also in part because of the widely differing requirements with regard to both cooking liquor composition and load on the recovery over the whole range of sulfite pulping processes from high yield semi-chemical pulps to low yield dissolving pulps. And, this is in part because of the varying interrelationship

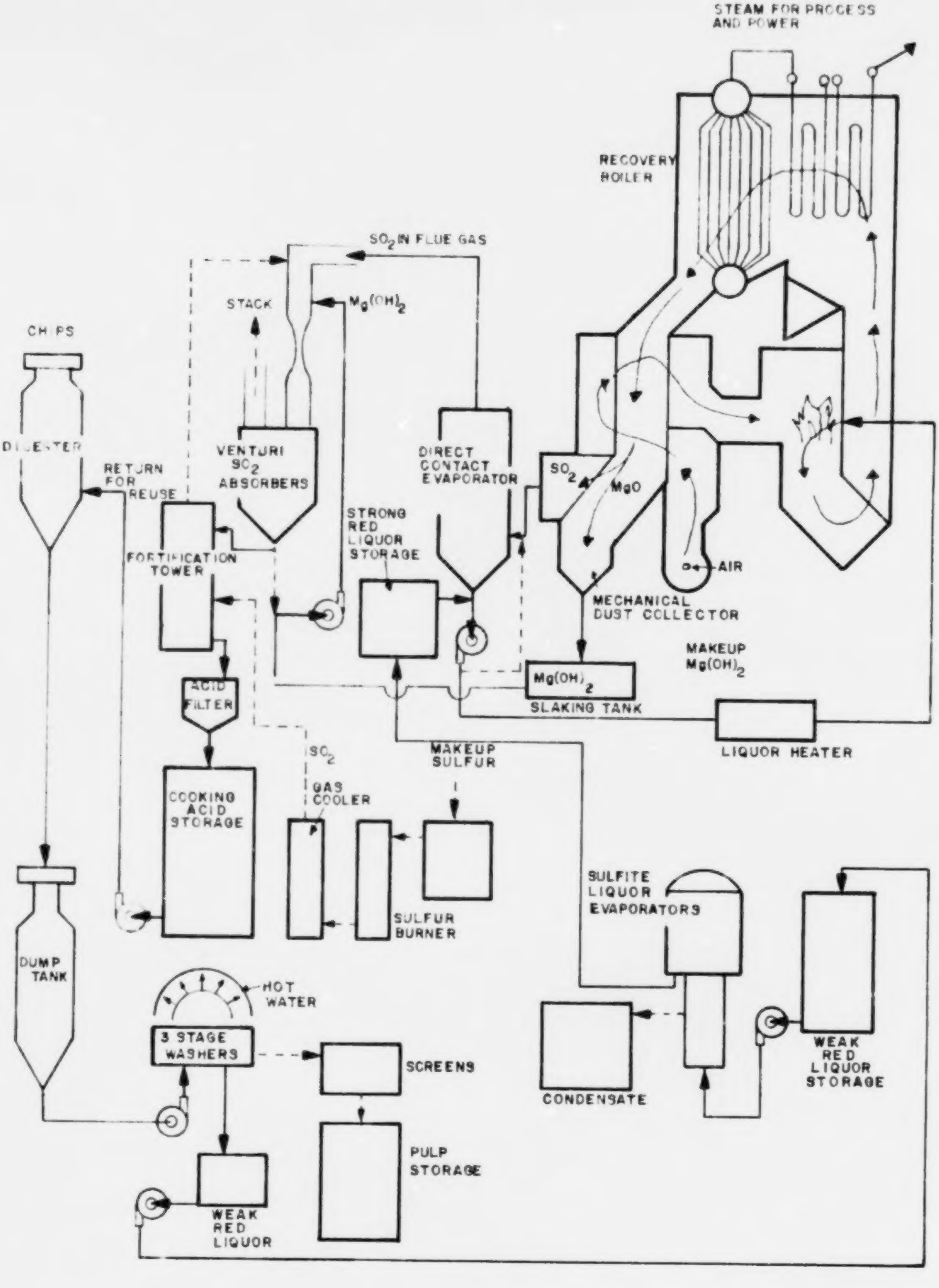

STEAM FOR PROCESS AND POWER
RECOVERY BOILER
SO2 IN FLUE GAS
STACK
Mg(OH)2
CHIPS
DIGESTER
VENTURI SO2 ABSORBERS
RETURN FOR REUSE
DIRECT CONTACT EVAPORATOR
SO2
MgO
FORTIFICATION TOWER
STRONG RED LIQUOR STORAGE
AIR
MECHANICAL DUST COLLECTOR
MAKEUP Mg(OH)2
Mg(OH)2
SLAKING TANK
ACID FILTER
LIQUOR HEATER
SO2
MAKEUP SULFUR
COOKING ACID STORAGE
GAS COOLER
SULFUR BURNER
SULFITE LIQUOR EVAPORATORS
DUMP TANK
HOT WATER
3 STAGE WASHERS
SCREENS
CONDENSATE
WEAK RED LIQUOR STORAGE
PULP STORAGE
WEAK RED LIQUOR

FIGURE 3-30. MAGNESIUM BISULFITE PROCESS FLOW

of technical, ecological, and economic factors for each installation, as a function of size and location as well as of special situations, such as integration with other pulping processes or the manufacture of by-products. It is, nevertheless, possible to draw some general conclusions regarding the present or probable trends in sulfite recovery, based on the information available today. It is believed that these choices represent the most direct solutions to the problem of eliminating air and stream pollution from spent sulfite liquors.

3.5.1 SULFUR RECOVERY ONLY

For small, independent, low combined acid sulfite mills with either calcium or ammonia base, the lowest cost solution would appear to be based upon recovery of heat values and the possible recovery of sulfur dioxide, but with no attempt at recovering the base for reuse. After concentration, both liquors may be burned in a conventional boiler equipped with a Loddby furnace or in a fluidized bed; and the sulfur dioxide may be recovered from digester blow gases and from the spent liquor prior to evaporation. When burning in a conventional furnace, adequate dust collection should be provided and for the ammonia base liquors, nitrogen oxides may present a problem at higher furnace temperatures. Both boiler and evaporator investments may be minimized by use of most of the recovered heat for direct contact liquor evaporation. For most paper-grade pulps, higher yields may be obtained with soluble bases, which should justify the use of ammonia base for small installations.

It might also be noted that Spring Chemicals, Ltd. has recently announced recoveries for calcium, magnesium or ammonia base acid sulfite or bisulfite liquors, with recovery of both the base and sulfur dioxide. The first step is precipitation of calcium as calcium sulfite, which reduces or eliminates scaling and also serves as the base recovery in calcium base pulping.

3.5.2 MAGNESIUM-BASE ONLY

For larger installations, use of magnesium or sodium with recovery of the base can be justified. The recovery of the magnesium base can be carried out by conventional (Babcock & Wilcox and Lenzing) or fluid bed (Copeland) combustion to give magnesium oxide in a form which may be reused in the process. These available recoveries are now well established; however, magnesium base systems are limited to pulping on the acid side and, therefore, are not suitable for the newer high strength alkaline sulfite pulping processes.

Sodium base may be used over the entire pulping pH range. In part, for this reason, there are a greater variety of sodium base recoveries with none so well established as those for magnesium base.

3.5.3 CROSS AND SALTCAKE RECOVERIES

Where location and capacities are suitable, the simplest sodium base "recovery" is combustion of the spent sulfite liquor as make-up with kraft liquor in the kraft recovery furnace (cross recovery). For small isolated mills, sodium base liquors may be burned in a fluid bed to produce by-product sodium carbonate and sodium sulfate, suitable for kraft make-up or as alkali in the manufacture of glass (Copeland and Dorr-Oliver).

3.5.4 CONVENTIONAL SODIUM RECOVERIES

The larger, independent sodium base pulp mills must have their own recoveries. The majority of present sodium base recoveries are based on the displacement of hydrogen sulfide from kraft-type green liquor with carbon dioxide, the combustion of the hydrogen sulfide to sulfur dioxide, and the recombination to form a pulping liquor (Sivola-Lurgi, Stora Kopparberg, and Tampella). One is based on so-called "shock pyrolysis" to separate sulfur as hydrogen sulfide from the sodium base, which is recovered as sodium carbonate (SCA-Billerud). Ion exchange is also practiced for partial recovery of sodium base (Ontario Paper Co.). Direct sulfitation of green liquor with recovery only of the base has also been used (IPC).

3.5.5 NEWER SODIUM-BASE RECOVERIES

In their more recent forms, sodium base sulfite recoveries are reported to be economically competitive with comparable magnesium base recoveries. They are also of the same order of cost as kraft recovery, in particular, where the higher yield of the sulfite pulp places a lower organic load on the recovery system. With further development of sulfite recovery systems, these costs should be further reduced. Several such systems are depicted in Figures 3-31 through 3-35.

Among such possible developments are bisulfite sulfitation (IPC), solid state carbonation (Mitsubishi), a new and simplified green liquor carbonation recovery (Owens-Illinois-Vulcan Cincinnati), direct oxidation of smelt or green liquor (Bratislava-Lurgi and Owens-Illinois), and fluid bed pyrolysis (Owens-Illinois).

3.6 SUMMARY OF AIR POLLUTION PROBLEMS

The terpene-like odors from the digesters and leaks of SO_2 in the various accumulators, storage tanks, washers, dump tanks, absorption towers, etc., are the normal sources of air pollution connected with sulfite pulp mills. Sulfur dioxide can readily be removed from gas streams with water scrubbers. Most sulfite mills in operation today find it economically sound to recover all the SO_2 possible.

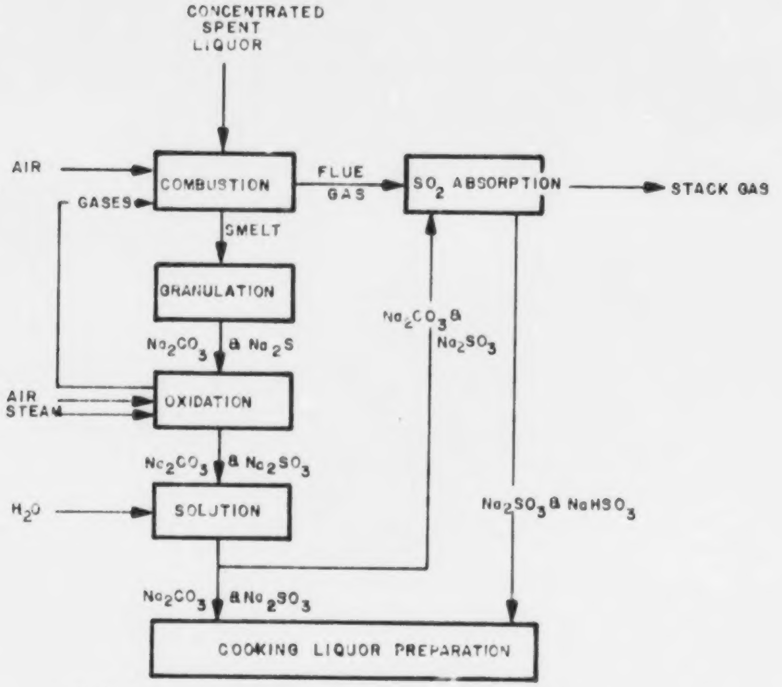

CONCENTRATED SPENT LIQUOR
AIR
COMBUSTION
GASES
FLUE GAS
SO_2 ABSORPTION
STACK GAS
SMELT
GRANULATION
Na_2CO_3 & Na_2S
Na_2CO_3 & Na_2SO_3
AIR
STEAM
OXIDATION
Na_2CO_3 & Na_2SO_3
H_2O
SOLUTION
Na_2SO_3 & $NaHSO_3$
Na_2CO_3 & Na_2SO_3
COOKING LIQUOR PREPARATION

FIGURE 3-31. DIRECT OXIDATION RECOVERY

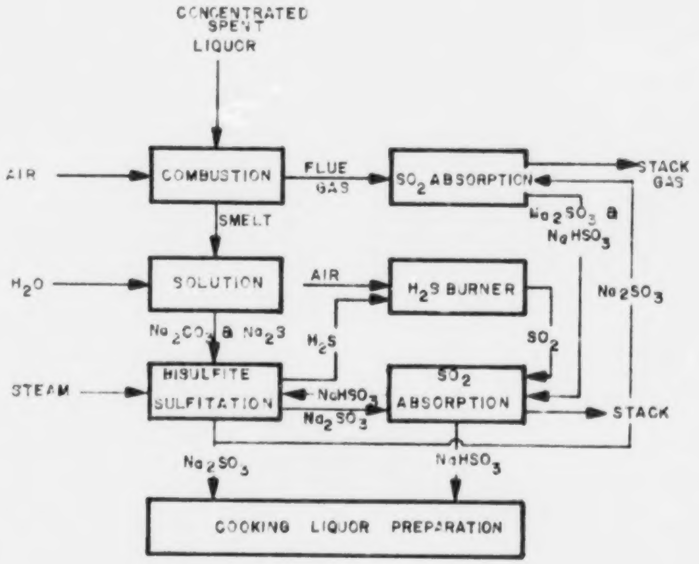

CONCENTRATED SPENT LIQUOR
AIR
COMBUSTION
FLUE GAS
SO_2 ABSORPTION
STACK GAS
SMELT
Na_2SO_3 & $NaHSO_3$
H_2O
SOLUTION
AIR
H_2S BURNER
Na_2SO_3
Na_2CO_3 & Na_2S
H_2S
SO_2
STEAM
BISULFITE SULFITATION
$NaHSO_3$
Na_2SO_3
SO_2 ABSORPTION
STACK
Na_2SO_3
$NaHSO_3$
COOKING LIQUOR PREPARATION

FIGURE 3-32. BISULFITE SULFITATION RECOVERY

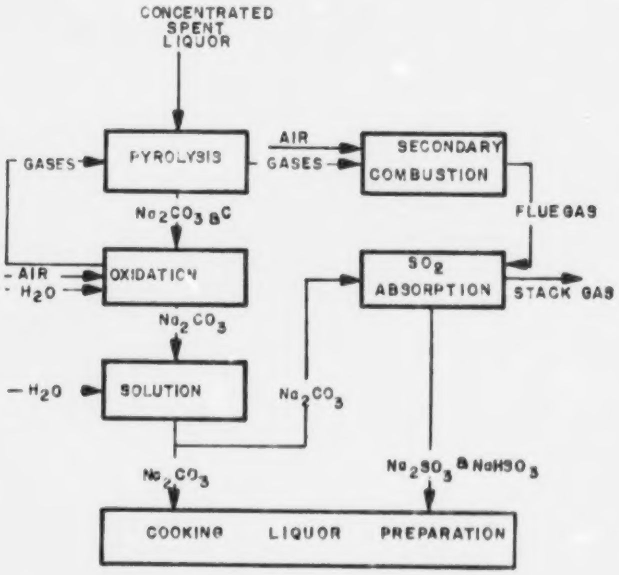

CONCENTRATED SPENT LIQUOR
GASES
PYROLYSIS
AIR
GASES
SECONDARY COMBUSTION
Na_2CO_3 & C
FLUE GAS
AIR
H_2O
OXIDATION
SO_2 ABSORPTION
STACK GAS
Na_2CO_3
H_2O
SOLUTION
Na_2CO_3
Na_2CO_3
Na_2SO_3 & $NaHSO_3$
COOKING LIQUOR PREPARATION

FIGURE 3-33. FLUID BED PYROLYSIS RECOVERY

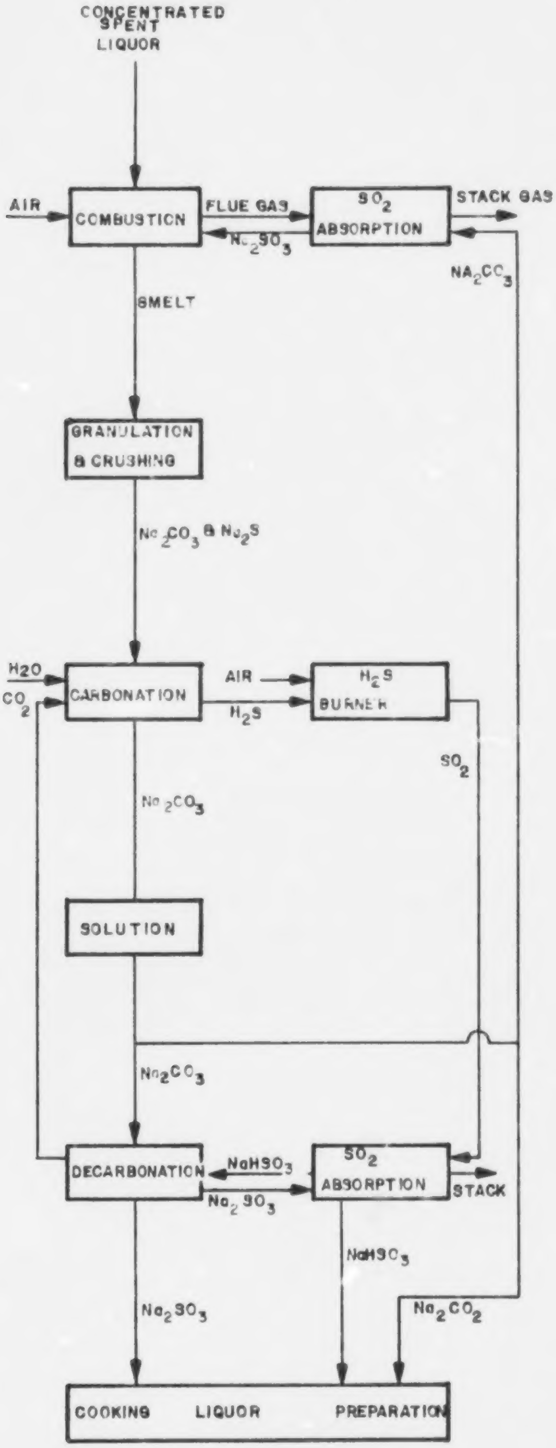

CONCENTRATED SPENT LIQUOR
AIR
COMBUSTION
FLUE GAS
SO_2 ABSORPTION
STACK GAS
Na_2SO_3
NA_2CO_3
SMELT
GRANULATION & CRUSHING
Na_2CO_3 & Na_2S
H2O
CO_2
CARBONATION
AIR
H_2S BURNER
H_2S
SO_2
Na_2CO_3
SOLUTION
Na_2CO_3
DECARBONATION
$NaHSO_3$
Na_2SO_3
SO_2 ABSORPTION
STACK
$NaHSO_3$
Na_2SO_3
Na_2CO_2
COOKING LIQUOR PREPARATION

FIGURE 3-34. SOLID CARBONATION RECOVERY

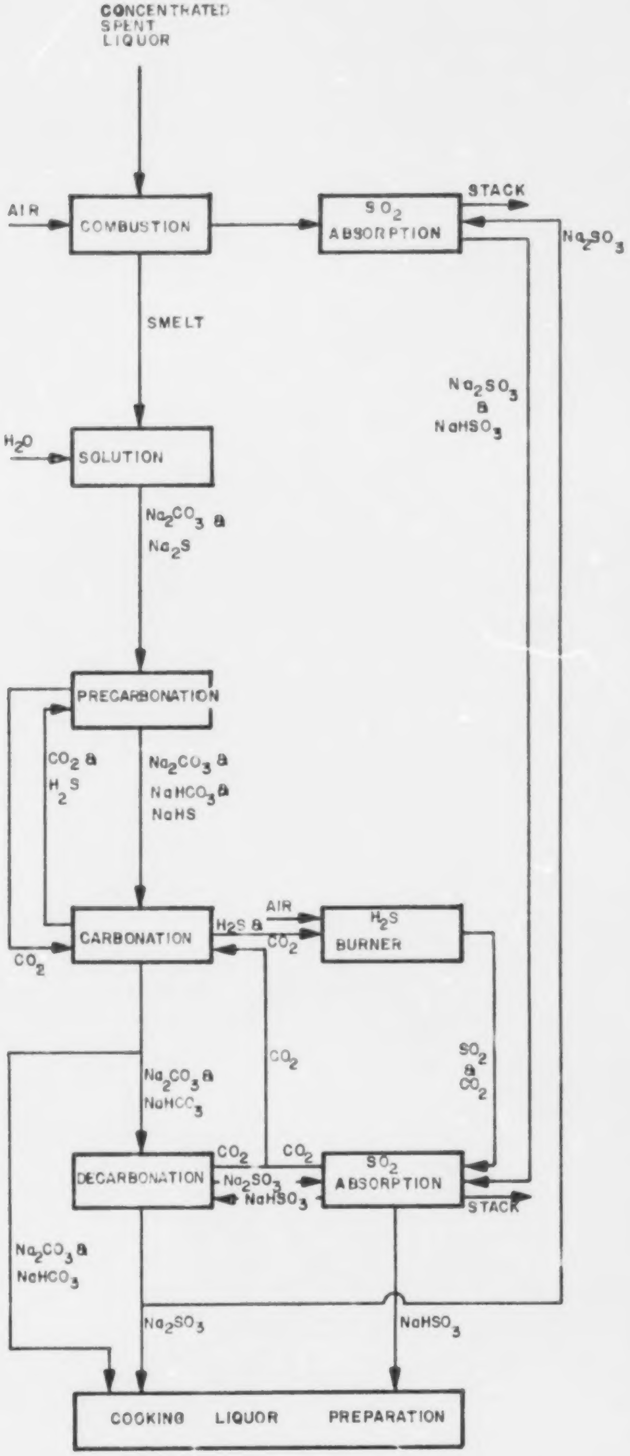

CONCENTRATED SPENT LIQUOR
AIR
COMBUSTION
SO_2 ABSORPTION
STACK
Na_2SO_3
SMELT
Na_2SO_3 & $NaHSO_3$
H_2O
SOLUTION
Na_2CO_3 & Na_2S
PRECARBONATION
CO_2 & H_2S
Na_2CO_3 & $NaHCO_3$ & NaHS
CARBONATION
CO_2
H_2S & CO_2
AIR
H_2S BURNER
CO_2
SO_2 & CO_2
Na_2CO_3 & $NaHCO_3$
DECARBONATION
CO_2
CO_2
Na_2SO_3
$NaHSO_3$
SO_2 ABSORPTION
STACK
Na_2CO_3 & $NaHCO_3$
Na_2SO_3
$NaHSO_3$
COOKING LIQUOR PREPARATION

FIGURE 3-35. GREEN LIQUOR CARBONATION RECOVERY

CHAPTER 4

MONITORING PROCESS AND CONTROL EQUIPMENT VARIABLES

This chapter presents those major process and control equipment variables that may be monitored with in-line instrumentation associated with modern wood pulping operations. The importance of the measurement of these variables as they relate to production and emission levels has been described in Chapter 3. In addition to standard on-line process instrumentation, applied to both process and control equipment, emission monitors for particulate and gaseous components that have proven application are discussed. Major emphasis has been placed on the kraft pulping process because of its dominance in the chemical wood pulping industry.

4.1 KRAFT PROCESS INSTRUMENTATION

Tables 4-1 and 4-2 in concert with Figures 4-1 through 4-13 depict instrumentation symbols and codes and standard kraft process flow sheets with superimposed in-line instrumentation.

The descriptions and depictions presented herein are for a kraft pulp mill and includes a typical bleaching operation. Although the kraft process was utilized for this illustration, the same approach would apply to both the sulfite and NSSC processes.

Table 4-1. Kraft Mill Instrument Applications.

DIGESTER ROOM

- Liquor drawdown and refill
- Total steam flow
- Heater condensate level
- Heater condensate conductivity
- Steaming
- Temperature-pressure
- Gas-off
- Blow tank level
- Turpentine condenser temperature
- Liquor circulation flow

BROWN STOCK WASHER

- Blow tank level
- Blow tank motor load dilution
- Stock to washer flow
- Knotter dilution
- Shower
- Filtrate tank level
- Repulper dilution
- Strong liquor baume
- Strong liquor filter
- Liquor to evaporator - flow
- Strong liquor storage level
- Washed stock storage level
- H. D. chest dilution

SCREEN ROOM

- Washed stock storage level
- Consistency
- Stock flow
- Dilution
- Screened stock storage level

BLEACH PLANT

- Screened stock storage level
- Consistency
- Chemical flow
- Tower levels
- Tower temperatures
- Dilution
- Mixer temperatures
- Shower flows
- Total steam flow
- Total water flow
- Fresh water make-up flow
- Filtrate overflow to sewer
- Bleach stock storage level
- H. D. storage dilution
- Chemical storage level
- Effluent to sewer - flow
- Hot water temperature

Table 4-1. Kraft Mill Instrument Applications. (Cont'd)

BLOW STEAM HEAT RECOVERY

Condenser temperature

Condenser water make-up temperature

Heat exchanger temperature

Clean hot water tank level

Clean hot water tank temperature

BLACK LIQUOR EVAPORATOR

Strong liquor storage level

Strong liquor baume

Flow ratio - liquor to 5 and 6 effects

Temperatures

Pressure and vacuum

Soap tank level

Steam flow and pressure

Boiling point rise

Condensate level

Thick liquor flash tank level

Condensate diversion

Thick liquor storage level

RECOVERY

Thick liquor storage level

Thick liquor flow

Cascade evaporator level

Precipitator wet bottom level

Multiple indicating draft gauge

Temperature in & out - cascade

Liquor-salt cake ratio

Primary heater temperature

Secondary heater temperature

Liquor to nozzles-pressure

Feed water control system

Oxygen

Steam temperature and pressure

Air flow

Dissolving tank density

Dissolving tank level

CAUSTICIZING

Liquor storage level

Raw green liquor flow

Green liquor temperature

Hot water temperature

Clarifier rake-torque

Water to lime mud filter

Lime mud density

Lime mud filter shower flow

Filter cake thickness

Lime mud filter vat - level

Table 4-1. Kraft Mill Instrument Applications.
(Cont'd)

CAUSTICIZING (continued)

White liquor flow

KILN

Oil temperature

Oil pressure

Oil storage level

Hot end temperature

Exit gas temperature

Draft control and gauge

Atomizing steam pressure

Kiln speed

Drive motor load

Scrubber level

CHEMICAL MAKE-UP AND HANDLING

Storage levels

Chlorine gas pressure

Chlorine vaporizer temperature

Caustic strength of solution

Strong caustic temperature

Hypo mixing

Chemical flows

Lime feeder

CHLORINE DIOXIDE PLANT

Chemical storage levels

Chemical mixing

Temperature

Cold water make-up

Spent liquor pH

Chlorine dioxide flow

High-low alarms

Table 4-2 TYPICAL LETTER INSTRUMENTATION SYMBOLS

		Measuring				Transmitting			Controlling							Alarm			
Process Variable	First letter	Indicating	Recording	Totalizing or integrating	Glass device for observation only	Blind	Indicating	Recording	Blind	Indicating	Recording	Self-actuated Valve	Safety valve	Control valve	Powered Operator	Blind	Indicating	Recording	Primary Elements
		-I	-R	-Q	-G	-T	-IT	-RT	-C	-IC	-RC	-CV	-SV	-V	-P	-A	-IA	-RA	-E
Analysis[a]	A-	AI	AR	AQ		AT	AIT	ART	AC	AIC	ARC			AV	AP	AA	AIA	ARA	AE
Burner Flame	B-	BI				BT	BIT		BC	BIC				BV	BP	BA	BIA		BE
Consistency	C-	CI	CR			CT	CIT	CRT	CC	CIC	CRC			CV	CP	CA	CIA	CRA	CE
Density	D-	DI	DR			DT	DIT	DRT	DC	DIC	DRC			DV	DP	DA	DIA	DRA	DE
Electric[b]	E-	EI	ER	EQ		ET	EIT	ERT	EC	EIC	ERC	ECV		EV	EP	EA	EIA	ERA	EE
Flow[c]	F-	FI	FR	FQ	FG	FT	FIT	FRT	FC	FIC	FRC	FCV	FSV	FV	FP	FA	FIA	FRA	FE
Hand	H-	HI	HR						HC					HV	HP				
Level	L-	LI	LR		LG	LT	LIT	LRT	LC	LIC	LRC	LCV		LV	LP	LA	LIA	LRA	LE
Moisture	M-	MI	MR			MT	MIT	MRT	MC	MIC	MRC			MV	MP	MA	MIA	MRA	ME
Pressure[c]	P-	PI	PR			PT	PIT	PRT	PC	PIC	PRC	PCV	PSV	PV	PP	PA	PIA	PRA	PE
Speed	S-	S-	SR	SQ		ST	SIT	SRT	SC	SIC	SRC	SCV	SSV	SV	SP	SA	SIA	SRA	SE
Temperature[c]	T-	TI	TR			TT	TIT	TRT	TC	TIC	TRC	TCV	TSV	TV	TP	TA	TIA	TRA	TE
Viscosity	V-	VI	VR		VG	VT	VIT	VRT	VC	VIC	VRC			VV	VP	VA	VIA	VRA	VE
Weight[f]	W-	WI	WR	WQ		WT	WIT	WRT	WC	WIC	WRC	WCV		WV	WP	WA	WIA	WRA	WE

NOTES

[a] Readily recognized self-defining symbols such as CO_2, O_2, pH, and ORP may be used in place of A.

[b] Letter subscripts c (current), v (voltage), or w (power) may be used after E to designate type of measurement.

[c] Lower case letters r, d, and t may be inserted to distinguish ratio, difference, and time respectively.

[d] Q may also be used with letters I, R, and C where indicating, recording, or control functions also exist.

[e] Lower case letter subscripts l and h may be used to denote low or high alarm functions.

[f] If required note (a) could be expanded to cover any first letter, not in conflict with those listed, as long as a description for such a designation is part of the flow diagram.

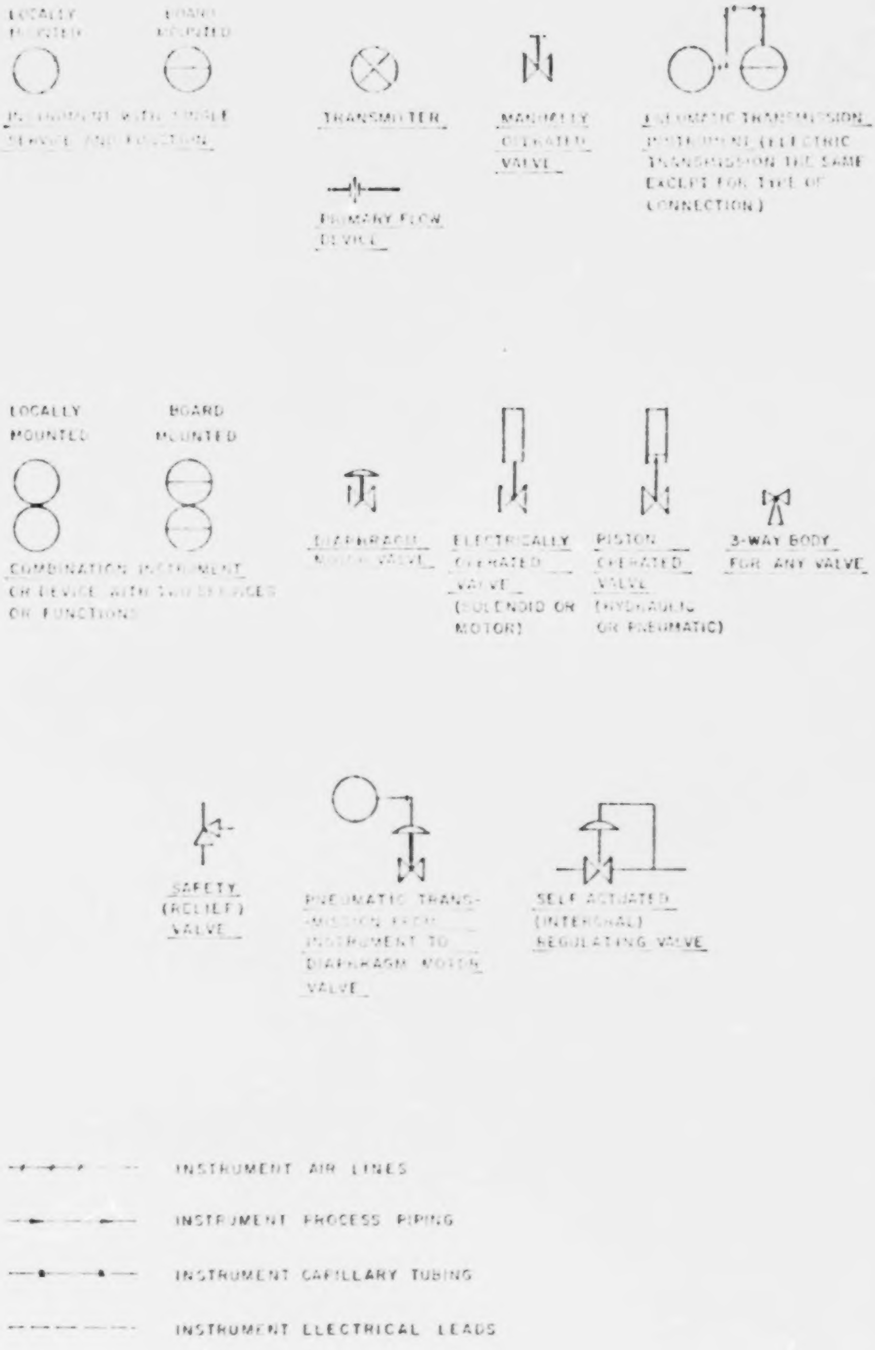
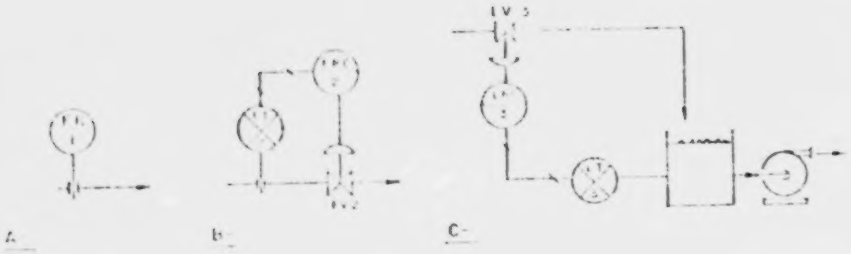

LOCALLY MOUNTED
BOARD MOUNTED
INSTRUMENT WITH SINGLE SERVICE AND FUNCTION
TRANSMITTER
PRIMARY FLOW DEVICE
MANUALLY OPERATED VALVE
PNEUMATIC TRANSMISSION INSTRUMENT (ELECTRIC TRANSMISSION THE SAME EXCEPT FOR TYPE OF CONNECTION)
LOCALLY MOUNTED
BOARD MOUNTED
COMBINATION INSTRUMENT OR DEVICE WITH TWO SERVICES OR FUNCTIONS
DIAPHRAGM MOTOR VALVE
ELECTRICALLY OPERATED VALVE (SOLENOID OR MOTOR)
PISTON OPERATED VALVE (HYDRAULIC OR PNEUMATIC)
3-WAY BODY FOR ANY VALVE
SAFETY (RELIEF) VALVE
PNEUMATIC TRANS-MISSION FROM INSTRUMENT TO DIAPHRAGM MOTOR VALVE
SELF ACTUATED (INTERNAL) REGULATING VALVE
INSTRUMENT AIR LINES
INSTRUMENT PROCESS PIPING
INSTRUMENT CAPILLARY TUBING
INSTRUMENT ELECTRICAL LEADS

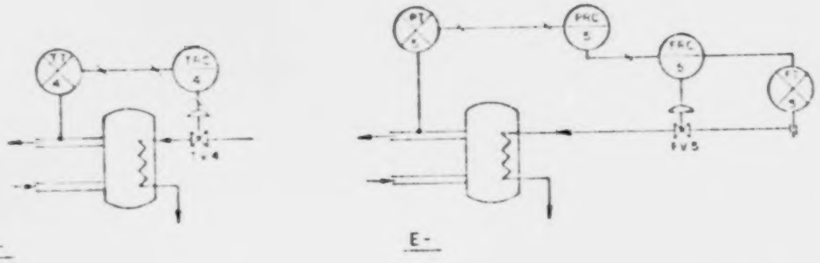
FIGURE 4-1 TYPICAL PICTORIAL INSTRUMENTATION SYMBOLS


LV 3
FR 1
FRC 2
FV 2
LT 3
A-
B-
C-

A- LOCALLY MOUNTED FLOW RECORDER

B- FLOW TRANSMITTER WITH PNEUMATIC TRANSMISSION TO BOARD-MOUNTED FLOW RECORDING CONTROLLER

C- LEVEL TRANSMITTER WITH PNEUMATIC TRANSMISSION TO BOARD-MOUNTED LEVEL RECORDER CONTROLLER


TT 4
TRC 4
TV 4
PT
PRC 5
FRC 5
FT 5
FV 5
D-
E-

D- TEMPERATURE TRANSMITTER WITH PNEUMATIC TRANSMISSION TO BOARD-MOUNTED TEMPERATURE RECORDER CONTROLLER

E- CASCADE CONTROL LOOP PRESSURE RECORDER CONTROLLER SETS FLOW RECORDER CONTROLLER

FIGURE 4-2 TYPICAL BASIC INSTRUMENT DIAGRAMS

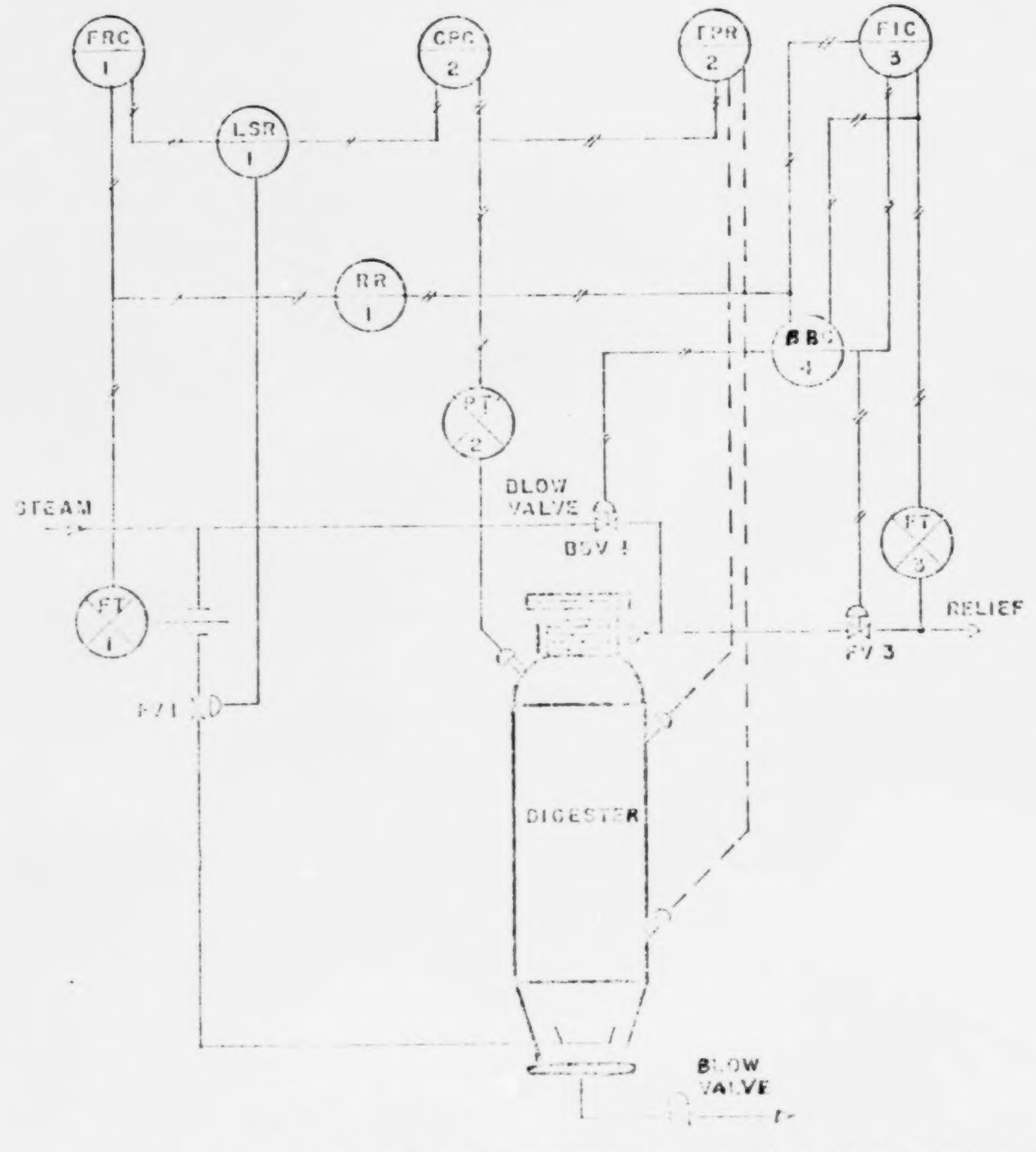

FRC 1
CPC 2
TPR 2
FIC 3
LSR 1
RR 1
BBC 4
PT 2
STEAM
BLOW VALVE
BSV 1
FT 1
FY 1
FT 3
FY 3
RELIEF
DIGESTER
BLOW VALVE

FIGURE 4-3 INSTRUMENTATION FOR KRAFT BATCH DIGESTER

FT-1	STEAM FLOW TRANSMITTER
FRC-1	STEAM FLOW RECORDING CONTROLLER
LSR-1	LOW SELECTOR RELAY
RR 1	REVERSING RELAY
FY-1	STEAM FLOW CONTROL VALVE
PT 2	DIGESTER PRESSURE TRANSMITTER
CPC 2	CAM PRESSURE CONTROLLER
TPR 2	DIGESTER TEMP. PRESS. RECORDER
FT 3	RELIEF FLOW TRANSMITTER
FIC 3	RELIEF FLOW INDICATING CONTROLLER
BBC-4	BLOW BACK CONTROLLER
BBV-4	BLOW BACK CONTROL VALVE

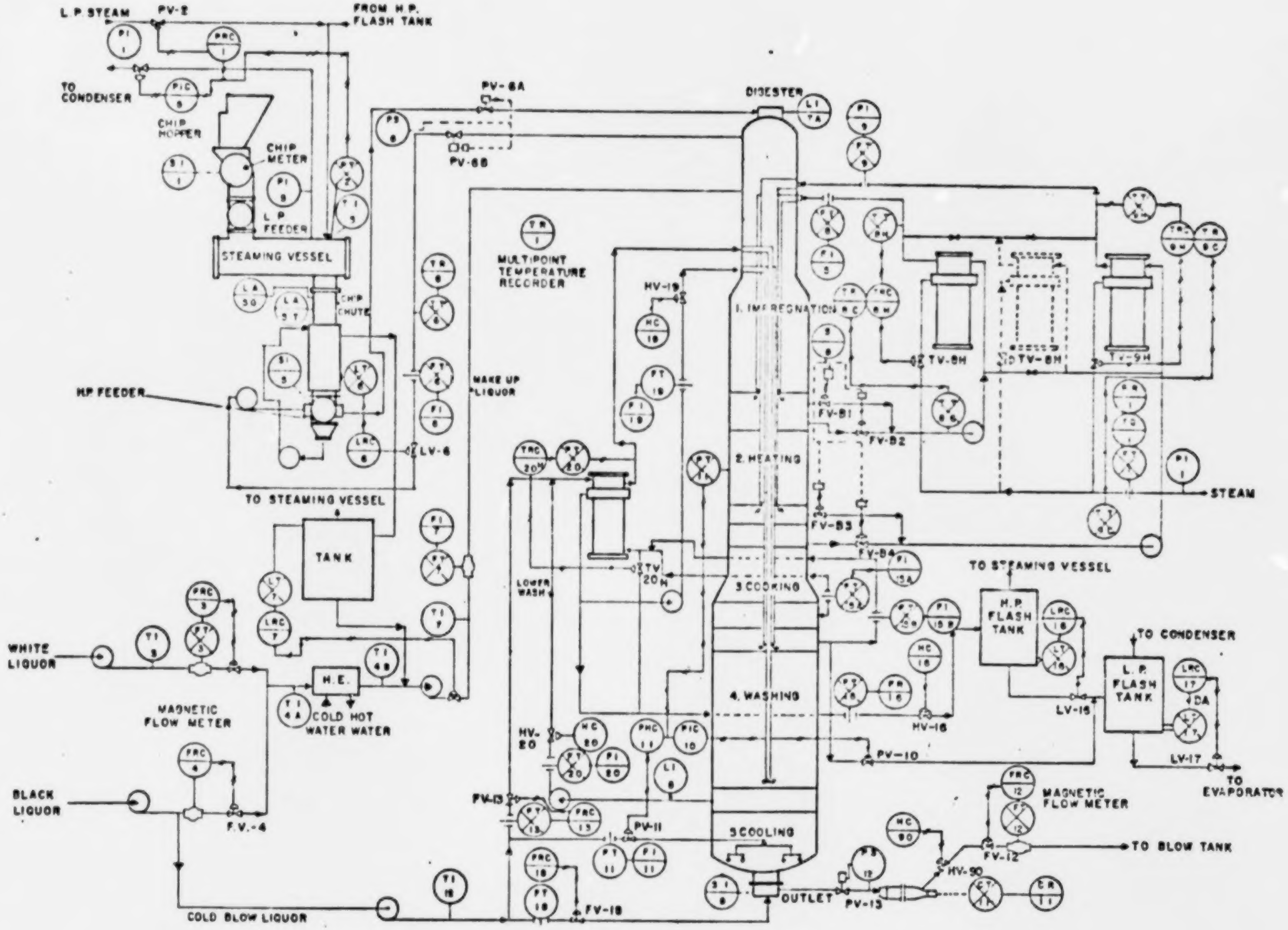

L.P. STEAM
PV-2
FROM H.P. FLASH TANK
TO CONDENSER
CHIP HOPPER
CHIP METER
L.P. FEEDER
STEAMING VESSEL
CHIP CHUTE
HP FEEDER
LV-6
TO STEAMING VESSEL
TANK
PV-8A
PV-8B
DIGESTER
MULTIPOINT TEMPERATURE RECORDER
MAKE UP LIQUOR
HV-19
1. IMPREGNATION
2. HEATING
3 COOKING
4. WASHING
5 COOLING
OUTLET
TV-8H
TV-8H
TV-9H
FV-B1
FV-B2
FV-B3
FV-B4
STEAM
TV 20H
LOWER WASH
TO STEAMING VESSEL
H.P. FLASH TANK
L.P. FLASH TANK
TO CONDENSER
LV-15
LV-17
TO EVAPORATOR
HV-16
PV-10
HV-20
PV-13
PV-11
FV-18
MAGNETIC FLOW METER
FV-12
HV-90
PV-13
TO BLOW TANK
WHITE LIQUOR
BLACK LIQUOR
MAGNETIC FLOW METER
F.V.-4
H.E.
COLD WATER
HOT WATER
COLD BLOW LIQUOR

FIGURE 4-4 INSTRUMENTATION FOR A CONTINUOUS DIGESTER

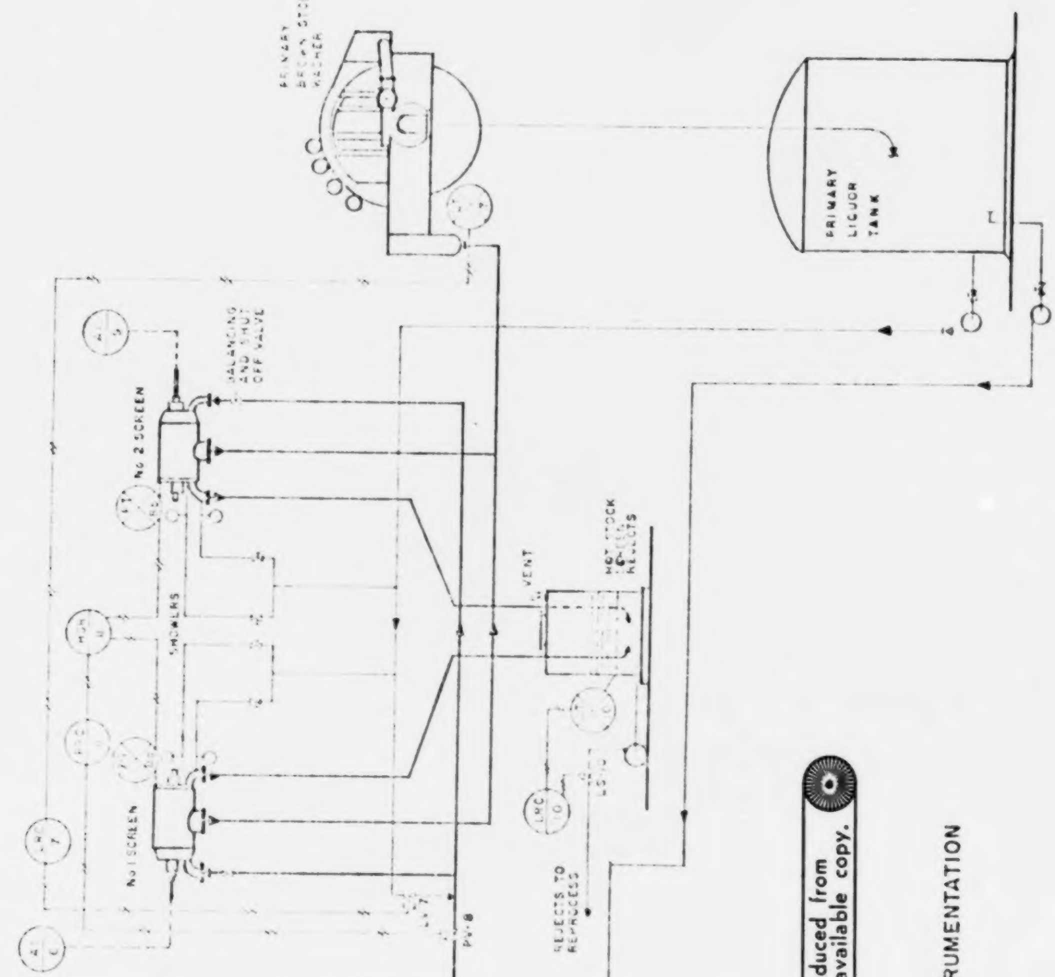

PRIMARY BROWN STOCK WASHER
PRIMARY LIQUOR TANK
No 2 SCREEN
BALANCING AND SHUT OFF VALVE
SHOWERS
No 1 SCREEN
VENT
HOT STOCK REJECTS
REJECTS TO REPROCESS
PV-8
PRIMARY DILUTION
LOW VOLUME SECONDARY DILUTION
WATER PURGE

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FIGURE 4-5 HOT STOCK SCREENING INSTRUMENTATION

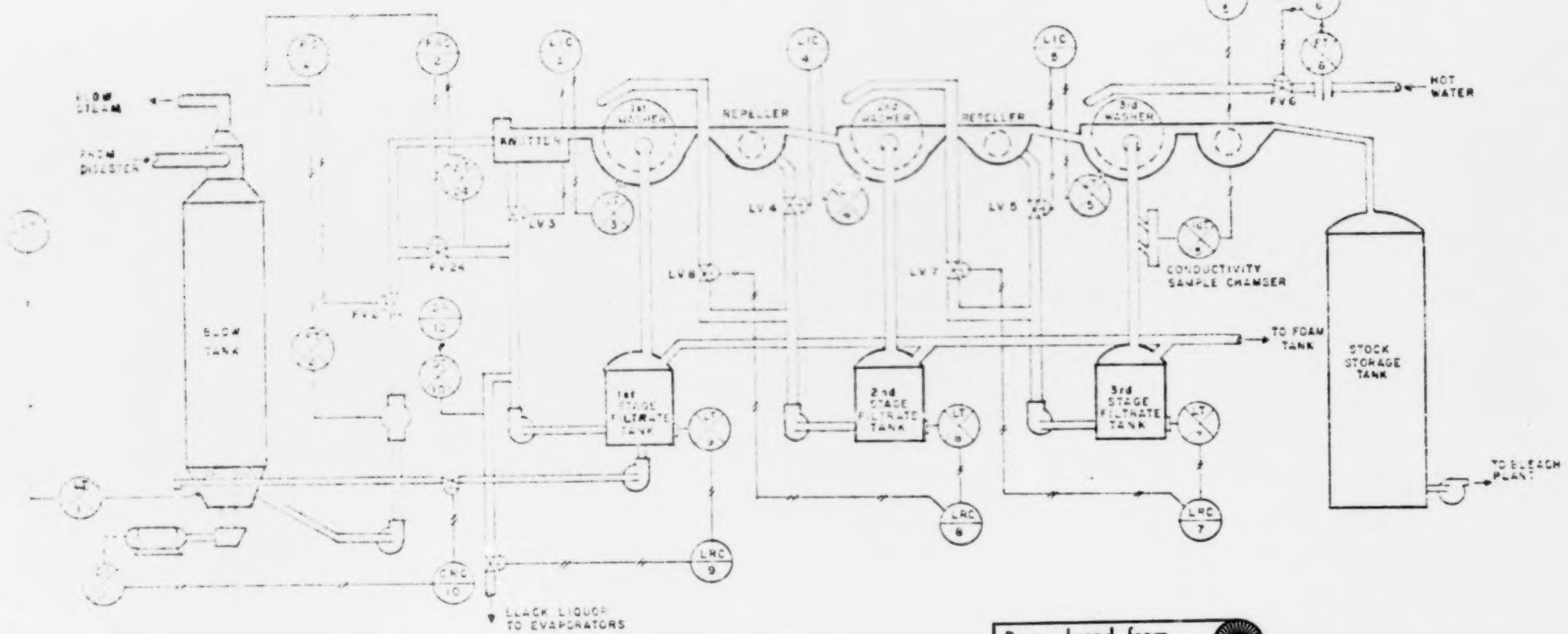
BLOW STEAM
FROM DIGESTER
BLOW TANK
FRC 2
LIC 3
LIC 4
LIC 5
CDRC 5
FRC 6
FT 6
FVG
HOT WATER
KNOTTER
1st WASHER
REPELLER
2nd WASHER
REPELLER
3rd WASHER
LV 3
LV 4
LV 5
LV 7
LV 8
FV 24
FV 2
DT 10
CRC 10
LT 3
CONDUCTIVITY SAMPLE CHAMBER
TO FOAM TANK
1st STAGE FILTRATE TANK
2nd STAGE FILTRATE TANK
3rd STAGE FILTRATE TANK
STOCK STORAGE TANK
LT
LRC 9
LRC 6
LRC 7
BLACK LIQUOR TO EVAPORATORS
TO BLEACH PLANT

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FIGURE 4-6 PULP WASHER INSTRUMENTATION

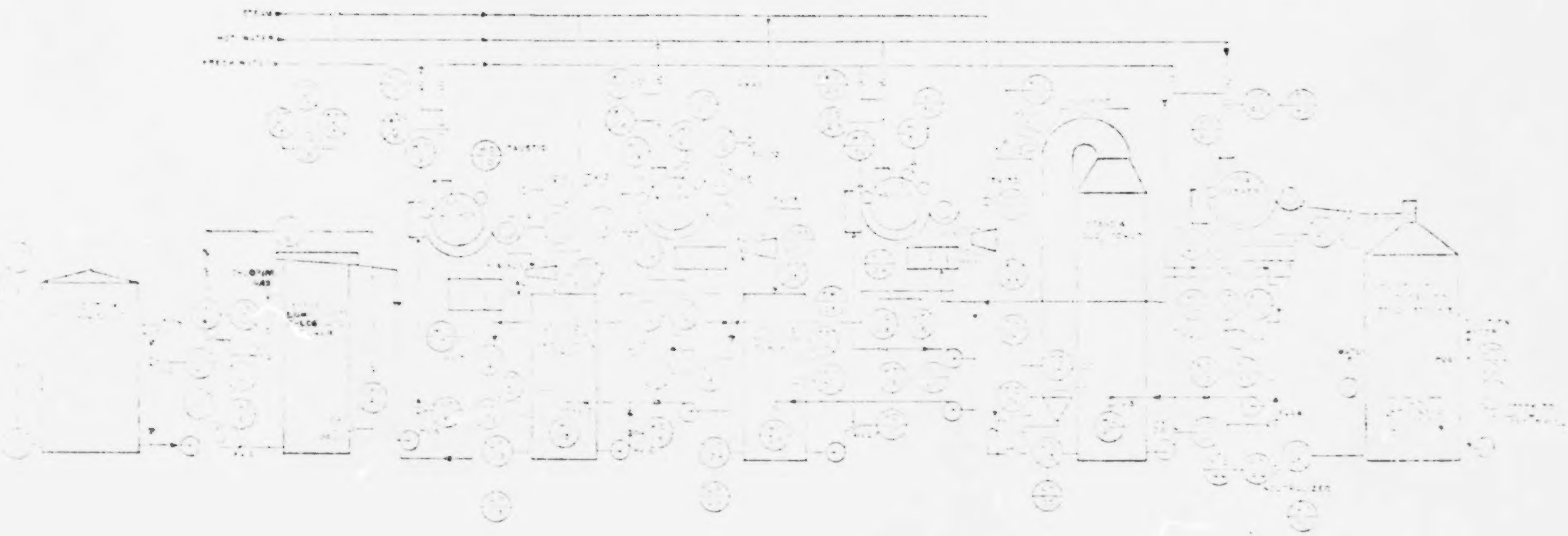
STEAM
HOT WATER
FRESH WATER
CAUSTIC
CHLORINE GAS

FIGURE 4-7 FOUR-STAGE BLEACH PLANT INSTRUMENTATION

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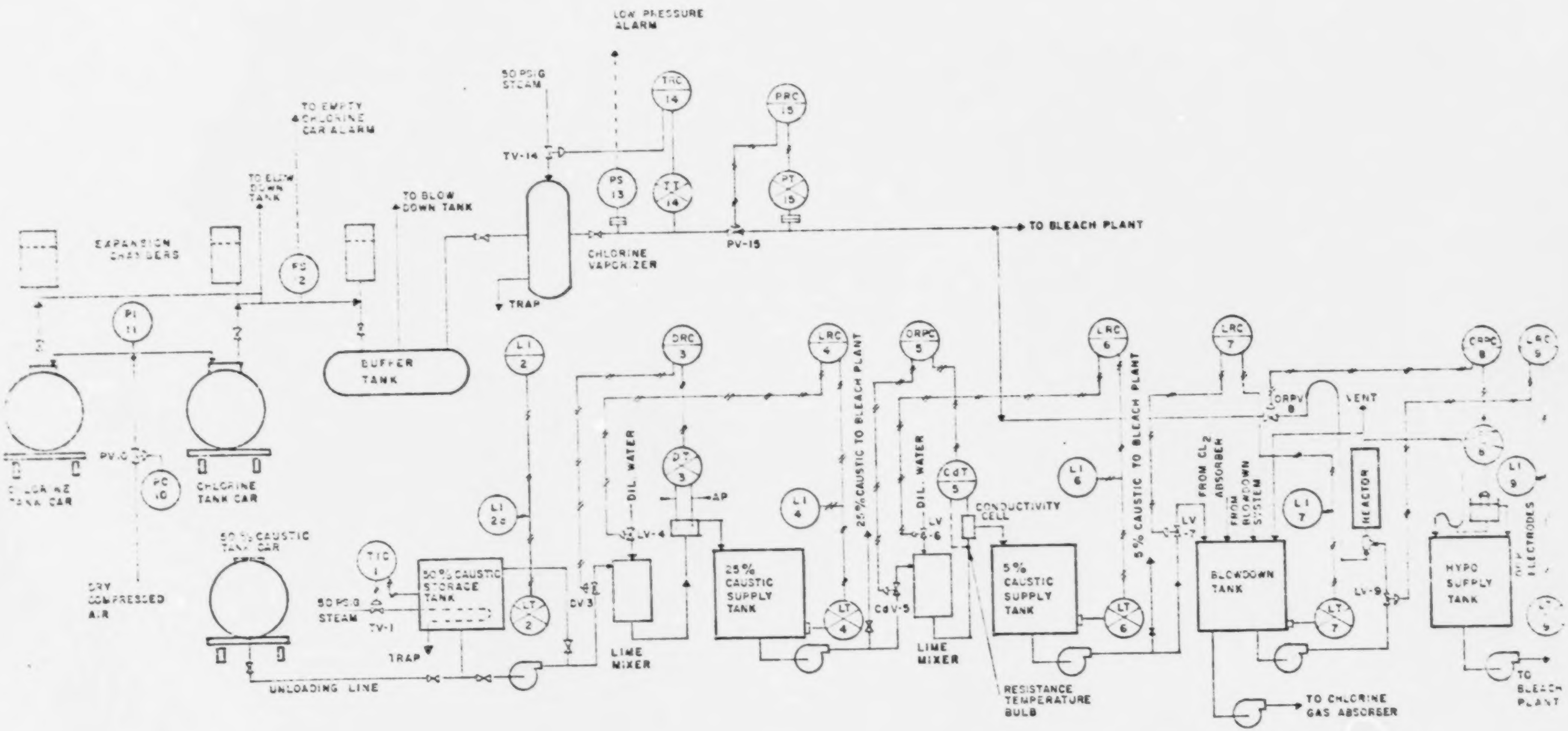
LOW PRESSURE ALARM
50 PSIG STEAM
TRC 14
PRC 15
TO EMPTY CHLORINE CAR ALARM
TV-14
TO BLOW DOWN TANK
PS 13
TT 14
PT 15
TO BLOW DOWN TANK
EXPANSION CHAMBERS
FS 2
CHLORINE VAPORIZER
PV-15
TO BLEACH PLANT
TRAP
PI 11
BUFFER TANK
LI 2
DRC 3
LRC 4
25% CAUSTIC TO BLEACH PLANT
ORPC 5
LRC 6
5% CAUSTIC TO BLEACH PLANT
LRC 7
ORPV 8
VENT
ORPC 8
LRC 9
DIL WATER
DT 3
ΔP
LI 4
DIL. WATER
CdT 5
LI 6
FROM CL2 ABSORBER
FROM BLOWDOWN SYSTEM
LI 7
REACTOR
LI 9
CHLORINE TANK CAR
PV-10
PC 10
CHLORINE TANK CAR
LI 2a
LV-4
LV 6-6
CONDUCTIVITY CELL
LV 7
ELECTRODES
50% CAUSTIC TANK CAR
TIC 1
50% CAUSTIC STORAGE TANK
DV 3
25% CAUSTIC SUPPLY TANK
5% CAUSTIC SUPPLY TANK
BLOWDOWN TANK
HYPO SUPPLY TANK
DRY COMPRESSED AIR
50 PSIG STEAM
TV-1
LT 2
LT 4
CdV-5
LT 6
LT 7
LV-9
TRAP
LIME MIXER
LIME MIXER
UNLOADING LINE
RESISTANCE TEMPERATURE BULB
TO CHLORINE GAS ABSORBER
TO BLEACH PLANT

FIGURE 4-8 SODIUM HYPOCHLORITE BLEACH LIQUOR PREPARATION INSTRUMENTATION.

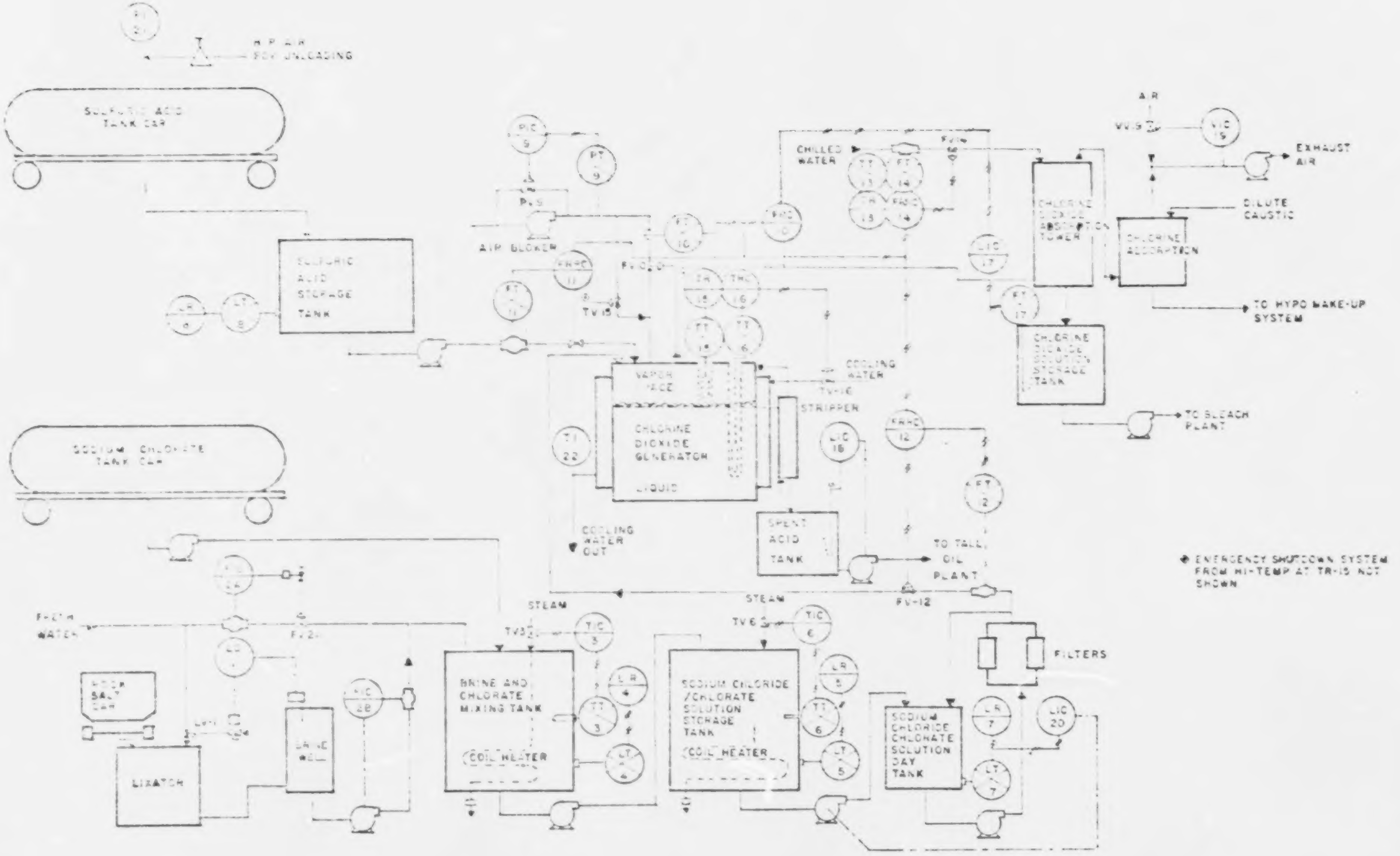
H.P. AIR FOR UNLOADING
SULFURIC ACID TANK CAR
SULFURIC ACID STORAGE TANK
SODIUM CHLORATE TANK CAR
AIR BLOWER
CHILLED WATER
COOLING WATER
STRIPPER
VAPOR SPACE
CHLORINE DIOXIDE GENERATOR
LIQUID
COOLING WATER OUT
SPENT ACID TANK
TO TALL OIL PLANT
CHLORINE DIOXIDE ABSORPTION TOWER
CHLORINE ABSORPTION
DILUTE CAUSTIC
EXHAUST AIR
AIR
TO HYPO MAKE-UP SYSTEM
CHLORINE DIOXIDE SOLUTION STORAGE TANK
TO BLEACH PLANT
FRESH WATER
ROCK SALT CAR
LIXATOR
BRINE WELL
STEAM
BRINE AND CHLORATE MIXING TANK
COIL HEATER
SODIUM CHLORIDE /CHLORATE SOLUTION STORAGE TANK
SODIUM CHLORIDE CHLORATE SOLUTION DAY TANK
FILTERS
FV-12
TV3
TV6
TV15
TV16
LIC 16
LIC 17
LIC 20
FRHC 10
FRHC 11
FRHC 12
FT 10
FT 11
FT 12
FT 17
PIC 9
PT 9
TT 6
TI 22
TIC 3
TIC 6
LR 4
LR 5
LR 7
LT 4
LT 5
LT 7
LT 8
VIC 15
♦ EMERGENCY SHUTDOWN SYSTEM FROM HI-TEMP AT TR-15 NOT SHOWN

FIGURE 4-9 CHLORINE DIOXIDE BLEACH LIQUOR PREPARATION INSTRUMENTATION

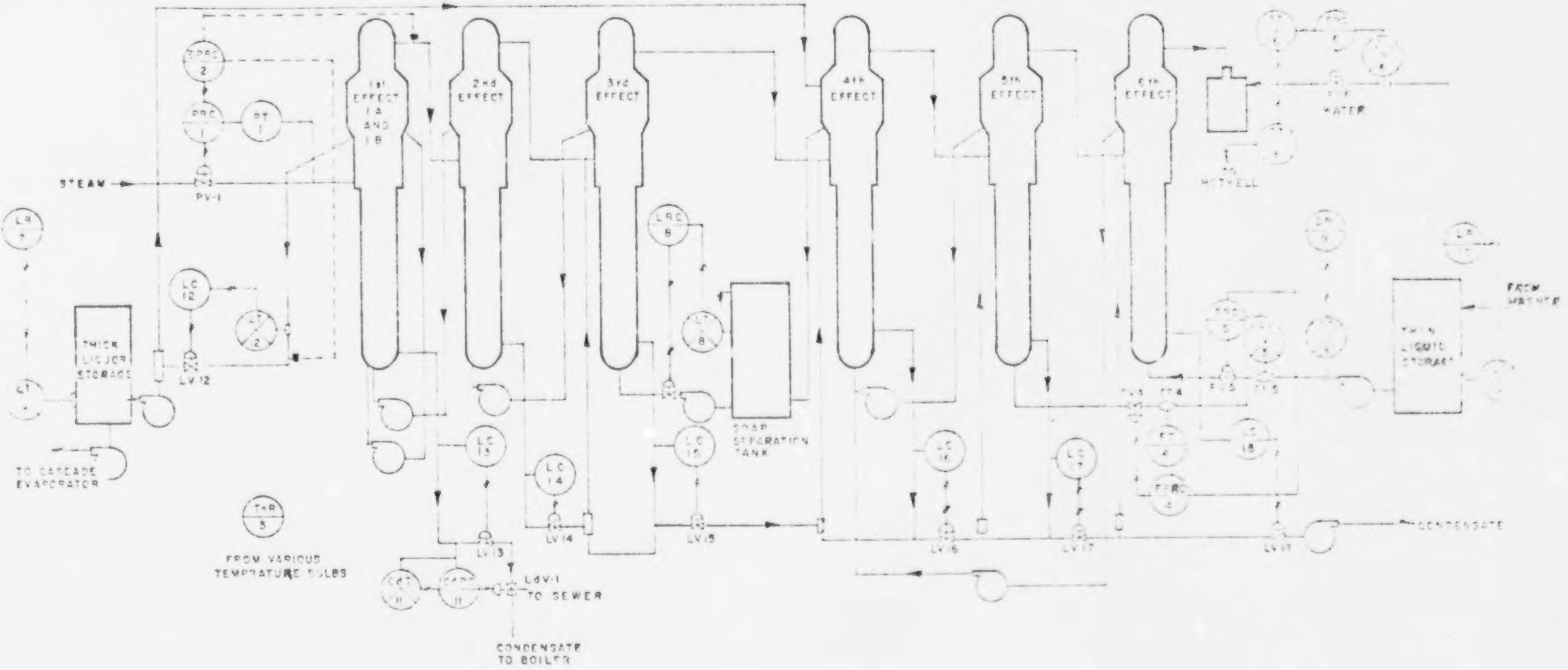
STEAM
EPRC 2
PRC 1
PT 1
PV-1
LR 7
LT 7
THICK LIQUOR STORAGE
TO CASCADE EVAPORATOR
LC 12
LT 12
LV 12
TRR 3
FROM VARIOUS TEMPRATURE BULBS
1st EFFECT 1A AND 1B
2nd EFFECT
3rd EFFECT
4th EFFECT
5th EFFECT
6th EFFECT
LC 13
LV 13
CdT 11
CdRC 11
LdV-1
TO SEWER
CONDENSATE TO BOILER
LC 14
LV 14
LRC 8
LT 8
LC 15
LV 15
SOAP SEPARATION TANK
LC 16
LV 16
LC 17
LV 17
FV4
FT4
FT 4
FFRC 4
FV5
FT5
LC 18
FRC 5
WATER
TO HOTWELL
LR
FROM WASHER
THIN LIQUID STORAGE
CONDENSATE

FIGURE 4-10 INSTRUMENTATION FOR MULTIPLE-EFFECT EVAPORATOR SYSTEM

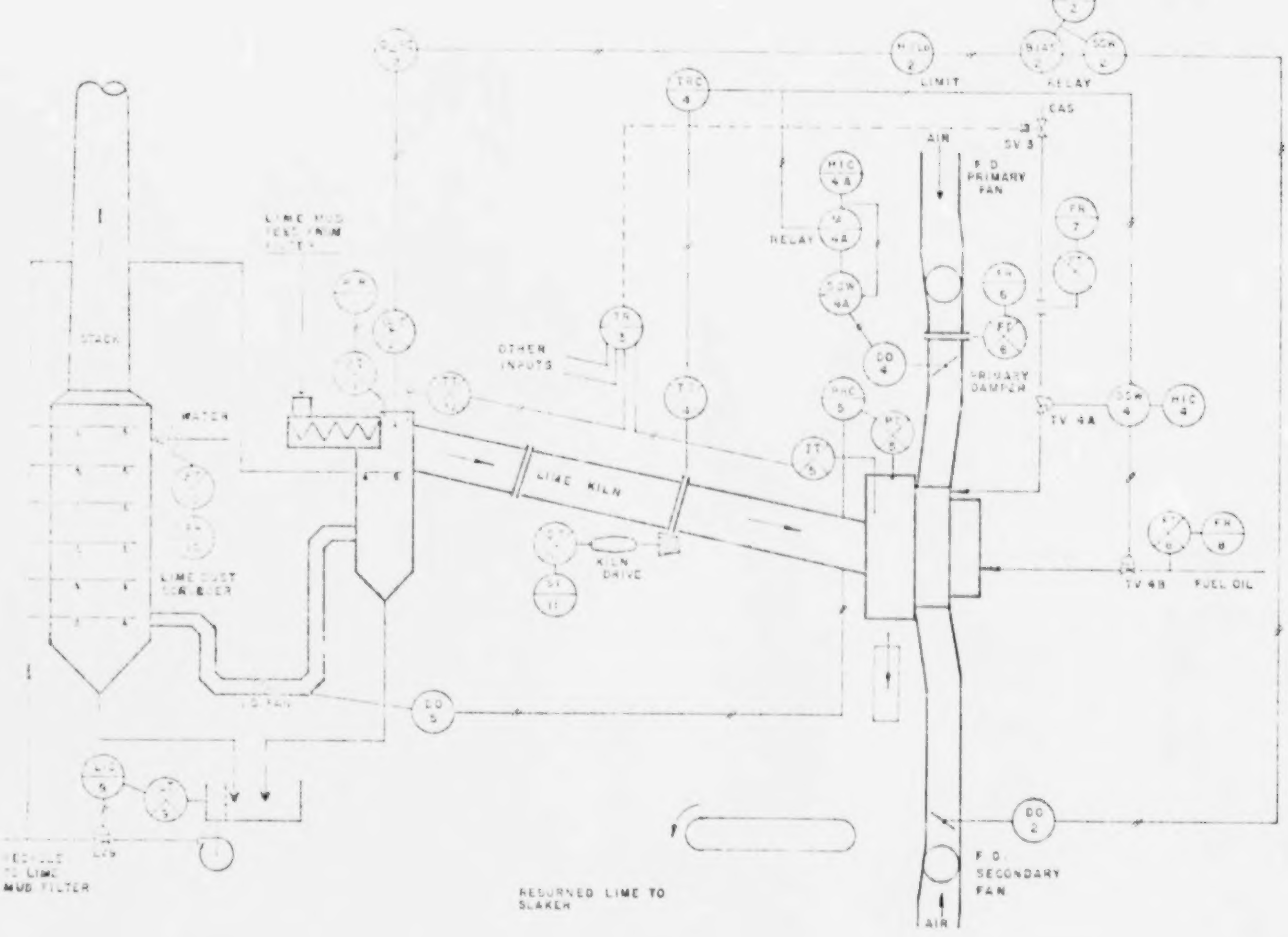
TRC
4
HIC
2
BIAS
2
SGW
2
2
LIMIT
RELAY
GAS
SV 3
AIR
F.D.
PRIMARY
FAN
HIC
4A
M
4A
RELAY
SGW
4A
DO
4
FR
7
FR
6
FT
6
PRIMARY
DAMPER
TV 4A
SGW
4
HIC
4
RHC
5
IT
5
TR
3
OTHER
INPUTS
TT
4
FR
8
TV 4B
FUEL OIL
DO
2
F.D.
SECONDARY
FAN
AIR
LIME MUD
FEED FROM
FILTER
STACK
WATER
LIME DUST
SCRUBBER
LIME KILN
KILN
DRIVE
ST
11
DO
5
I.D. FAN
LIC
5
RECYCLE
TO LIME
MUD FILTER
RESURNED LIME TO
SLAKER

FIGURE 4-11 INSTRUMENTATION TO CONTROL COMBUSTION IN THE LIME RECOVERY PROCESS.

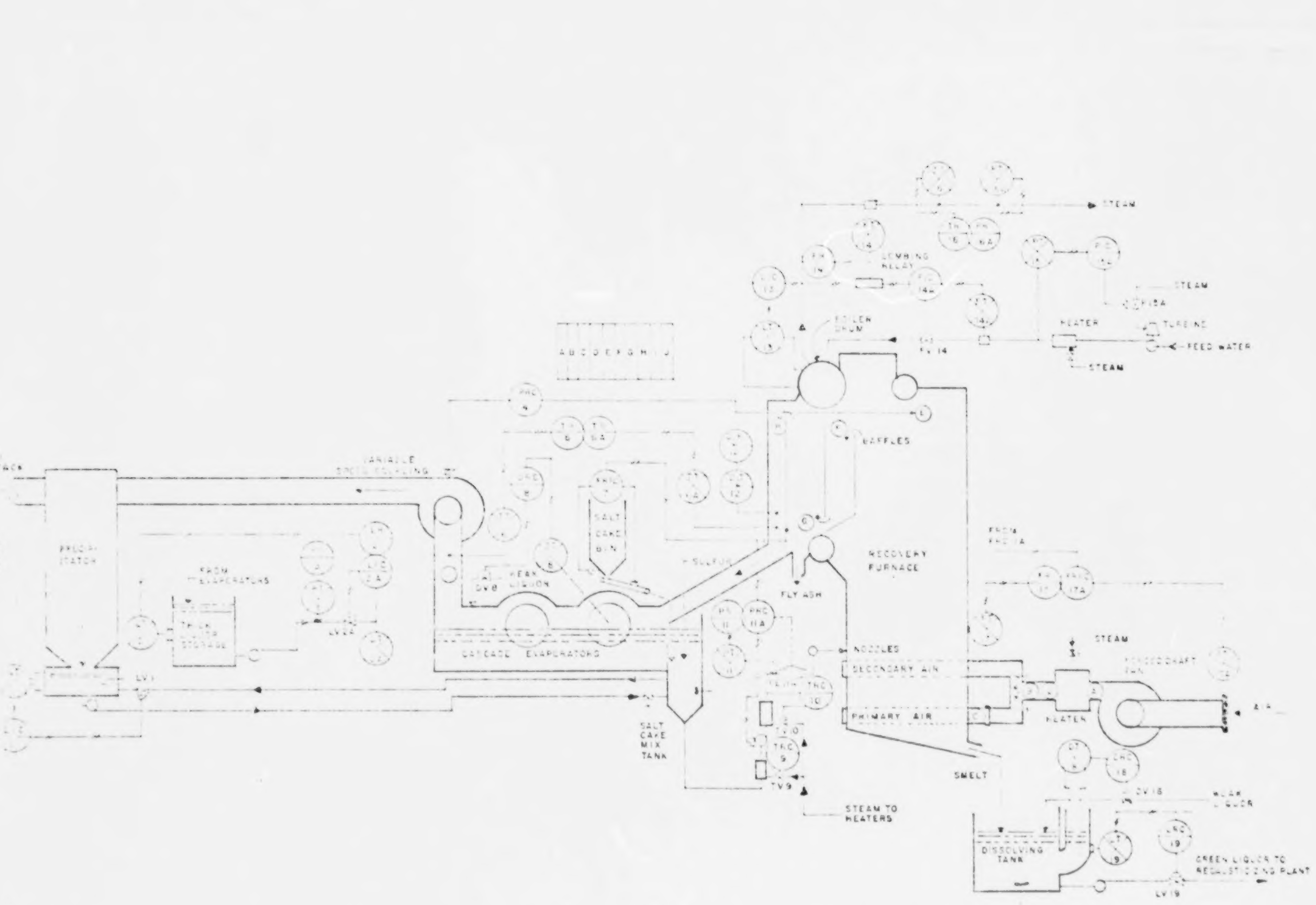
TO STACK
PRECIPITATOR
FROM EVAPORATORS
THICK LIQUOR STORAGE
LV1
LV2A
VARIABLE SPEED COUPLING
WEAK LIQUOR
DV8
SALT CAKE BIN
CASCADE EVAPORATORS
SALT CAKE MIX TANK
SULFUR
FLY ASH
A B C D E F G H I J
BOILER DRUM
LEVELING RELAY
BAFFLES
RECOVERY FURNACE
NOZZLES
SECONDARY AIR
PRIMARY AIR
SMELT
STEAM TO HEATERS
TV9
STEAM
HEATER
TURBINE
FEED WATER
FV 14
FROM PRC 1A
FORCED DRAFT FAN
AIR
DISSOLVING TANK
WEAK LIQUOR
DV18
GREEN LIQUOR TO RECAUSTICIZING PLANT
LV19
PRC 4
PRC 11A
TRC 9
TRC 10
LRC 19
DRC 18

FIGURE 4-12 SOME OF THE MORE IMPORTANT INSTRUMENTATION USED ON A HIGH CAPACITY RECOVERY FURNACE.

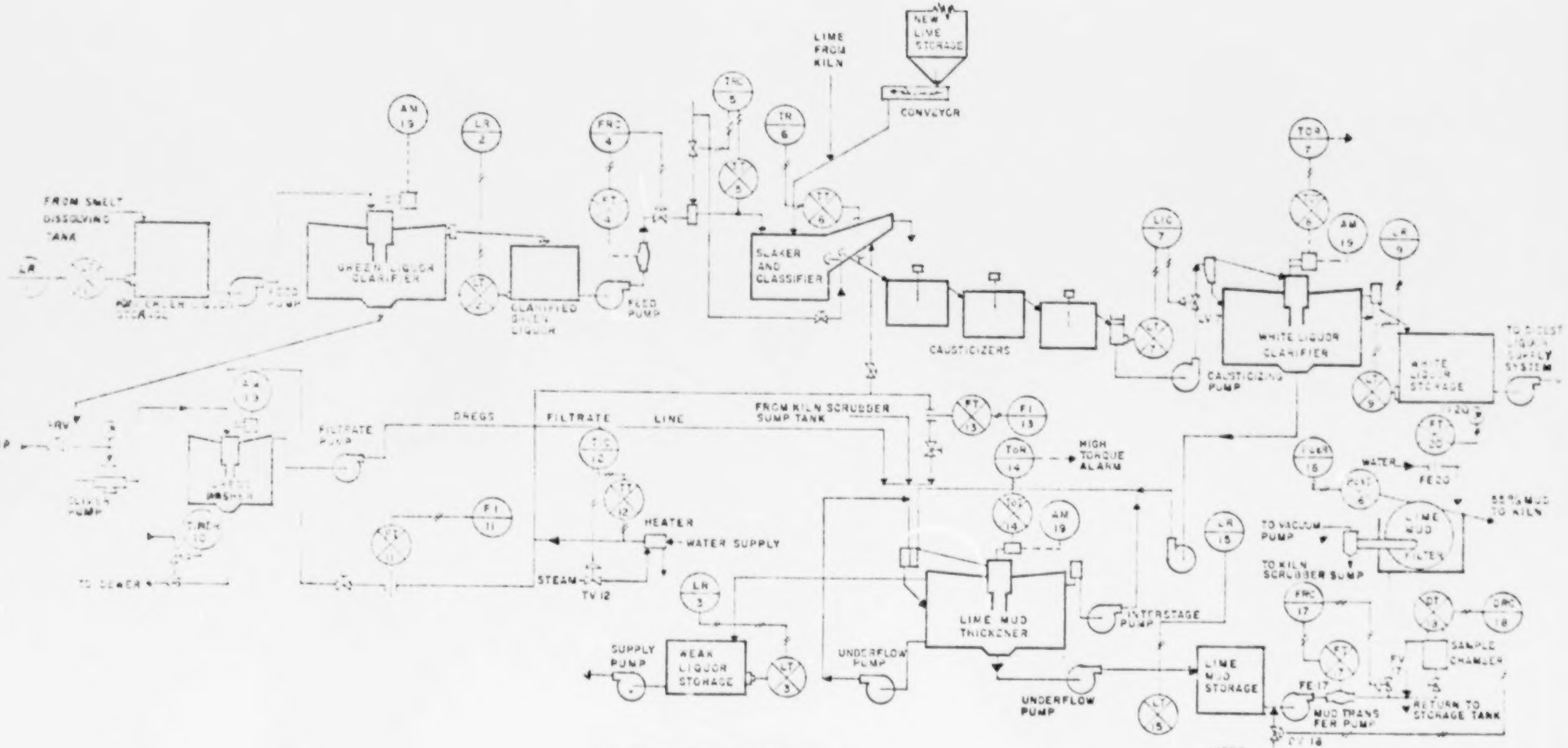
FROM SMELT DISSOLVING TANK
LR
GREEN LIQUOR STORAGE
FEED PUMP
AM 19
GREEN LIQUOR CLARIFIER
LR 2
CLARIFIED GREEN LIQUOR
FRC 4
FT 4
FEED PUMP
TRC 5
TT 5
IR 6
TT 6
LIME FROM KILN
NEW LIME STORAGE
CONVEYOR
SLAKER AND CLASSIFIER
CAUSTICIZERS
LIC 7
LT 7
CAUSTICIZING PUMP
TQR 7
AM 19
WHITE LIQUOR CLARIFIER
LR 9
LT 9
WHITE LIQUOR STORAGE
TO DIGEST LIQUOR SUPPLY SYSTEM
FT 20
FE 20
WATER
AIR
FRV
DREGS WASHER
DILVER PUMP
TIRCK 10
TO SEWER
FILTRATE PUMP
DREGS
FILTRATE
LINE
TIC 12
TT 12
HEATER
WATER SUPPLY
STEAM
TV 12
FI 11
FT 11
FROM KILN SCRUBBER SUMP TANK
FT 13
FI 13
TQR 14
HIGH TORQUE ALARM
AM 19
LR 3
SUPPLY PUMP
WEAK LIQUOR STORAGE
LT 3
UNDERFLOW PUMP
LIME MUD THICKENER
INTERSTAGE PUMP
UNDERFLOW PUMP
LR 15
LT 15
LIME MUD STORAGE
FE 17
MUD TRANSFER PUMP
WATER
CV 18
FRC 17
FT 17
FV 17
DT 18
DRC 18
SAMPLE CHAMBER
RETURN TO STORAGE TANK
TO VACUUM PUMP
TO KILN SCRUBBER SUMP
LIME MUD FILTER
55% MUD TO KILN

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FIGURE 4-13 TYPICAL INSTRUMENTATION FOR LIQUOR CAUSTICIZING IN ALKALINE COOKING.

4.2 INSTRUMENTATION FOR EMISSION MONITORING

There are three basic approaches to instrumented source monitoring. In the first, which may be called extractive, a continuous sample stream is drawn from the stack and transported to the analyzer, which can be mounted in any convenient location. This requires a probe mounted in the stack or duct, and some form of interface system to provide the analyzer with a sample that is in an appropriate state of cleanliness, temperature, pressure, and moisture content. This approach is the oldest and has provided the most experience to date.

The second approach may be called in-situ monitoring. The instrument is mounted either inside the plenum or just outside the stack. In the case of optical instruments, the source may be mounted on one side and the detector on the other, so that the instrument scans the full width of the stack. This method is most commonly used for visible particulates or "smoke." A combination of the first and second methods is to mount the analyzer directly on the stack and draw the sample through it with little or no preconditioning. Obviously, this requires an instrument that can accept the sample in its natural state.

The third approach is to monitor the plume above the stack with a remote optical instrument. So far, this approach is in the research stage, whereas the other two methods have been reduced to a more practical state.

The in-situ across-the-stack approach and the remote method offer an advantage over the extractive approach in that they provide an average reading rather than a point reading. However, it is theoretically feasible to use multiple extractive probes and obtain an integrated sample that is representative of the complete cross section.

The potential pollutants which may be measured continuously in a kraft pulp mill include sulfur dioxide, TRS, and particulate matter.

4.3 CONTINUOUS SULFUR DIOXIDE MONITORS

As previously stated, sulfur dioxide (SO_2) emissions arise from the oxidation of sulfur bearing compounds normally found in all three of the chemical wood pulping processes. Generally speaking, SO_2 emissions from the kraft process are limited to the recovery furnace and the ancillary power generating facilities. SO_2 emissions from the sulfite and NSSC processes can be significant from a standpoint of air pollution and reusable chemical losses. The following descriptions of continuous SO_2 monitoring systems can be adapted to any of the aforedescribed pulping processes.

Three methods have been used to monitor sulfur dioxide from the sulfite process. These methods include infrared and ultraviolet spectroscopy and conductivity.

A non-dispersive infrared analyzer has been used in a magnesium base acid bisulfite mill with success. The reference cell contained all of the flue gas components less the sulfur dioxide. The flue gas is passed through the sample cell at 3.5 CFH and the differential output is related to the SO_2 in the flue gas. The IR cell windows must be protected from water. In one instance, a large filter is followed by a refrigerated dryer reducing the flue gas to -10°F. Particulates in the flue gas caused frequent plugging of the sample line and the instrument environment was unduly corrosive for the electronic circuitry. It is estimated that one installation cost in excess of $10,500 and has been continually plagued with approximately 50 percent instrument downtime.

Thoen's ultraviolet system by contrast is quite simple in design, relatively inexpensive (less than $2,000), and extremely reliable. The ultraviolet source and detector are mounted externally to the flue gas duct and protected from the flue gas by quartz windows. A 2 1/2 inch diameter tube is located at 90° to the flue gas flow and connects the externally mounted source and detector. One-half inch holes are placed 2 1/2 inches apart at 90° to the gas flow. These physical arrangements minimize particulate and water accumulation in the light path tube. Maintenance is limited primarily to a cleaning of the quartz windows every three weeks. The instrument has been calibrated externally to the flue gas duct by passing nitrogen-sulfur dioxide mixtures through the light path tube. (Possibly a more reliable calibration procedure would involve the addition of known quantities of sulfur dioxide to a flue gas matrix rather than the nitrogen gas base which has been used.)

A variety of conductivity instruments from home-builts to modified commercial units have been successfully used by several sulfite mills. Conductivity units require close control of reagent and sample gas flow to maintain calibration. These instruments are relatively inexpensive.

Correlation spectrometry and multiple-scan interferometry have been proposed for use as remote sensing devices to determine the SO_2 concentration from industrial and power plant stacks. In theory the instrument could be used by the emitter at the source to monitor SO_2 emissions or by regulatory officials located in a mobile unit at some distance from the source. Significantly, this can also be done at night. This instrumentation is considerably more complex than Thoen's ultraviolet system. Thus initial expense and subsequent maintenance could be significantly greater.

4.4 GAS/LIQUID CHROMATOGRAPHIC ANALYSIS OF REDUCED SULFUR COMPOUNDS

Pulp mill emissions often contain an appreciable amount of water vapor, water droplets and particulate matter such as fiber, organic and inorganic chemicals and mists. Proper sample preparation and handling must precede injection of the sample into a chromatographic system. Sample conditioning requirements are dictated by the impurities which must be removed to protect the analytical equipment, or by necessity to maintain the physical properties of the gas so as to prevent a material alteration of the components of the gas stream. Consideration must, therefore, be given to (a) appropriate particulate and gas separation schemes, (b) sample collection and conveyance systems that do not react with the sample, and (c) sample collection and conveyance systems that maintain the sample above its dew-point temperature.

4.4.1 OPERATING PRINCIPLES

The function of a gas chromatographic system is twofold: (1) separation of the sample into its individual components, and (2) determination of desired isolated components with a suitable detector.

Separation of the sample into its components is effected by a chromatographic column. During analysis, a uniform flow of inert gas (commonly called carrier gas) is maintained in the system. A small volatile liquid or gas sample is injected into the inert gas stream prior to its entry into the column. As the sample components are carried through the column by the carrier gas stream, absorption and desorption from the liquid support proceeds in accordance with the individual component's coefficient of distribution. As the components are eluted from the column, quantitative analysis is performed by a detector which monitors a common property of the compounds. Retention time of the component in the column is used to qualitatively identify the compound and measured detector response is used to quantitatively identify the compound.

For proper operation of a gas-liquid chromatographic system, the sample handling system, injection technique, column and detector must be carefully selected for the specific application. Temperature and carrier gas flow control are also important items. Figure 4-14. a block diagram of a typical gas liquid chromatographic system.

4.4.2 SAMPLING SYSTEMS

The sample handling equipment must be constructed of materials which will not react with individual components of the gas stream to be analyzed. Those suitable for use in pulp mill situations dealing

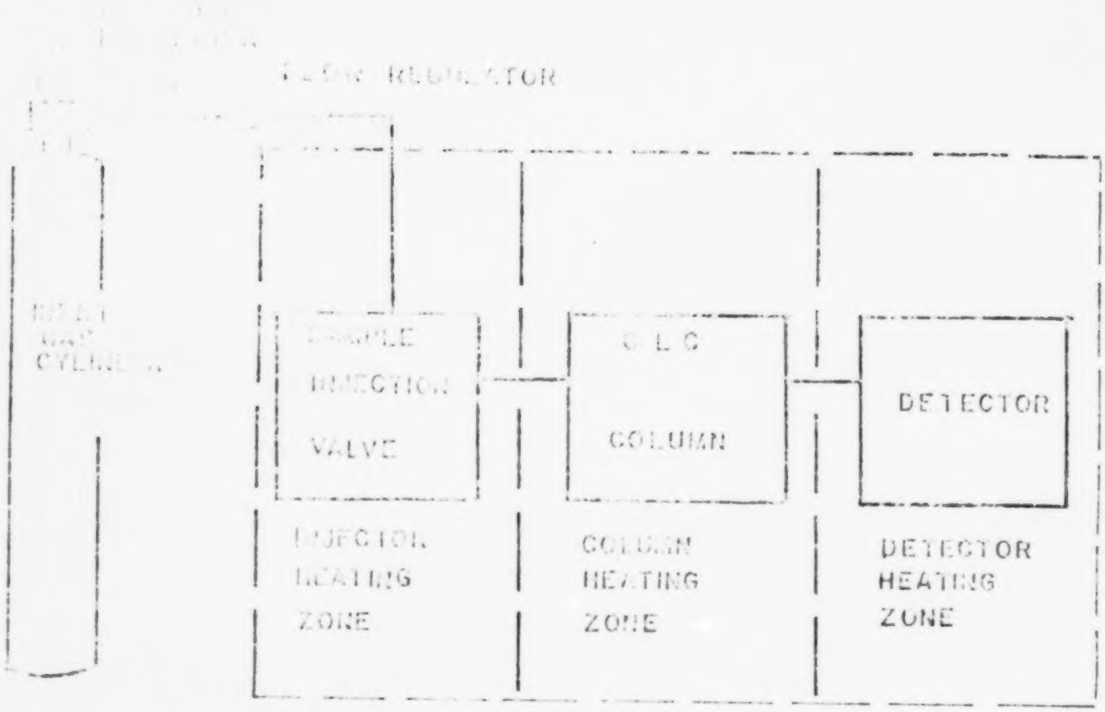

FLOW REGULATOR
INERT GAS CYLINDER
SAMPLE INJECTION VALVE
G L C COLUMN
DETECTOR
INJECTOR HEATING ZONE
COLUMN HEATING ZONE
DETECTOR HEATING ZONE

FIGURE 4-14 GAS CHROMATOGRAPHY SYSTEM

with sulfur gases, terpenes, and alcohols, in the one ppm volume basis (v/v) range, are listed below.

Teflon and glass are the least reactive of the materials listed and are preferred materials of construction for gas handling systems where batch samples are handled and where any absorbance or reaction may significantly alter the sample composition. Type 316 stainless steel is satisfactory for continuous flow systems, and after several exposures, because of saturation characteristics, is generally suitable for batch sample handling systems.

The other two materials, polyethylene and polypropylene must be used with care. They are sufficiently reactive to limit their use almost exclusively to continuous flow systems where any reaction between the construction material and a gas component alters the gas composition insignificantly.

CONSTRUCTION MATERIALS FOR GAS HANDLING SYSTEMS

Least Reactive	Teflon Glass
Satisfactory for Continuous Flow Systems	316 - Stainless Steel
Must be used with care	Polyethylene* Polypropylene

*Limited to temperatures of 250°F or less.

4.4.3 PREPARATION AND CONDITIONING

Many emission sources at the point of sampling contain liquid mists (a) which are not properly a portion of the sample since they are removed prior to discharge, or (b) for which no suitable system can be devised for their incorporation in the sample.

Even when judgement dictates these droplets should be a portion of the sample, their entry into a heated sampling system and subsequent evaporation may cause random, unpredictable and nonrepresentative gas concentrations in the sample stream. As a matter of course it is therefore a common practice to remove large liquid droplets from the gas stream before sampling.

These droplets can be removed by a properly designed entrainment separator on the end of the sample probe as illustrated in Figure 4-15.

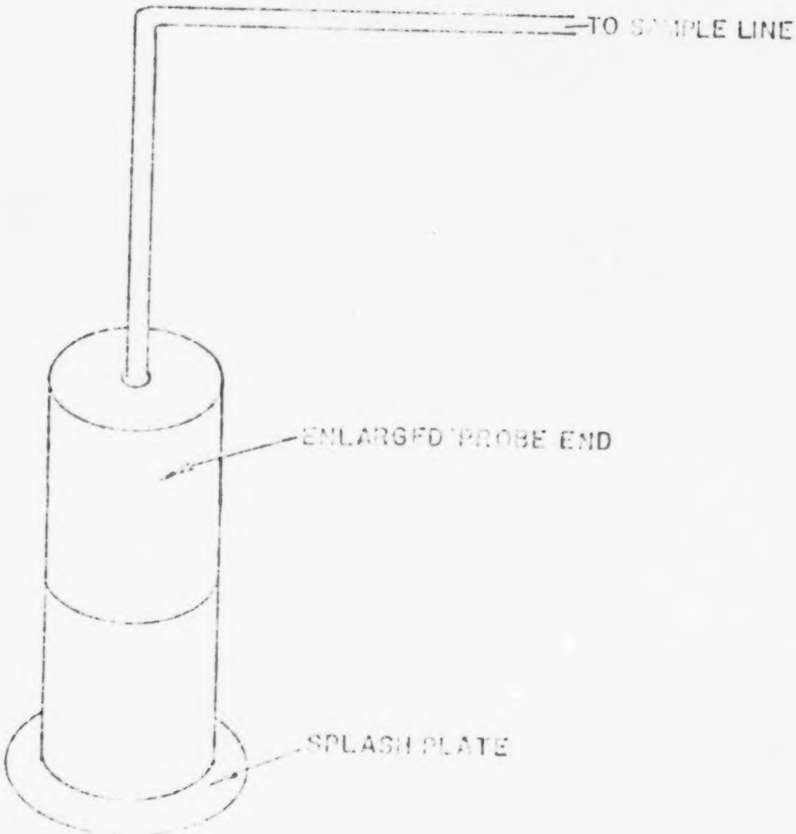

TO SAMPLE LINE
ENLARGED PROBE END
SPLASH PLATE

FIGURE 1-8. PROBE FOR OIL, [illegible] DISCHARGED WATER

With this device, water droplets are diverted by the splash plate and the small amount that circumvents the plate will fall by gravity from the enlarged low gas flow velocity area incorporated in the probe design. Nothing precludes the use of a properly designed cyclone for droplet removal providing it is located in the duct so that evaporation on heated surfaces of a transfer system can be avoided.

Coarse particulate removal is a requirement in all continuous sampling systems. Stainless steel tubes of 1 to 2 inches diameter and 6 to 12 inches long packed with glass wool have been used. Ceramic or sintered stainless steel diffuser tubes have also been used (1). Commercial probes are also available (1). Either manual or automatic blowback systems for cleaning are required if frequent removal from the stack for cleaning is to be avoided. The blowback cleaning system should isolate the probe from the remainder of the sampling system to avoid major surges in flow that may cause damage. Fine particulate filtration following coarse filtration is a common requirement on continuous flow gas handling systems. Walther and Amberg report the use of a commercially available system (2). One filter which removes particles down to one micron in size found extensive use for this purpose. A stainless steel body and sintered stainless steel filter cartridge make it well suited for use in systems heated above the gas dew point.

Water vapor is present in most emission sources at concentrations generally ranging from 20 to 95% (v/v). When cooled to ambient temperatures either (a) condensation occurs which entraps unknown and variable amounts of the components of primary interest, or (b) some of the components may be cooled below their boiling point resulting in their condensation. To prevent these occurrences the sample must be maintained above its dewpoint temperature. This can be done either by (a) using heat traced sampling equipment, or (b) dilution of the source gas to the point at which its dewpoint is below ambient temperature.

Even when dilution is used as a means to avoid condensation, seldom if ever can the use of a heated sampling line be completely avoided. Care must be taken to assure that the gas sample temperature remains above its dew point prior to dilution which normally involves some heat traced sampling line. The sample conditioning equipment for chromatographic analysis is listed below.

SAMPLE CONDITIONING EQUIPMENT

Sample Components	Sample Preparation Device
Liquid Droplets	Entrainment separators
Particulate	Coarse filtration and fine filtration
Water Vapor	Heated equipment - Dilution with an inert gas

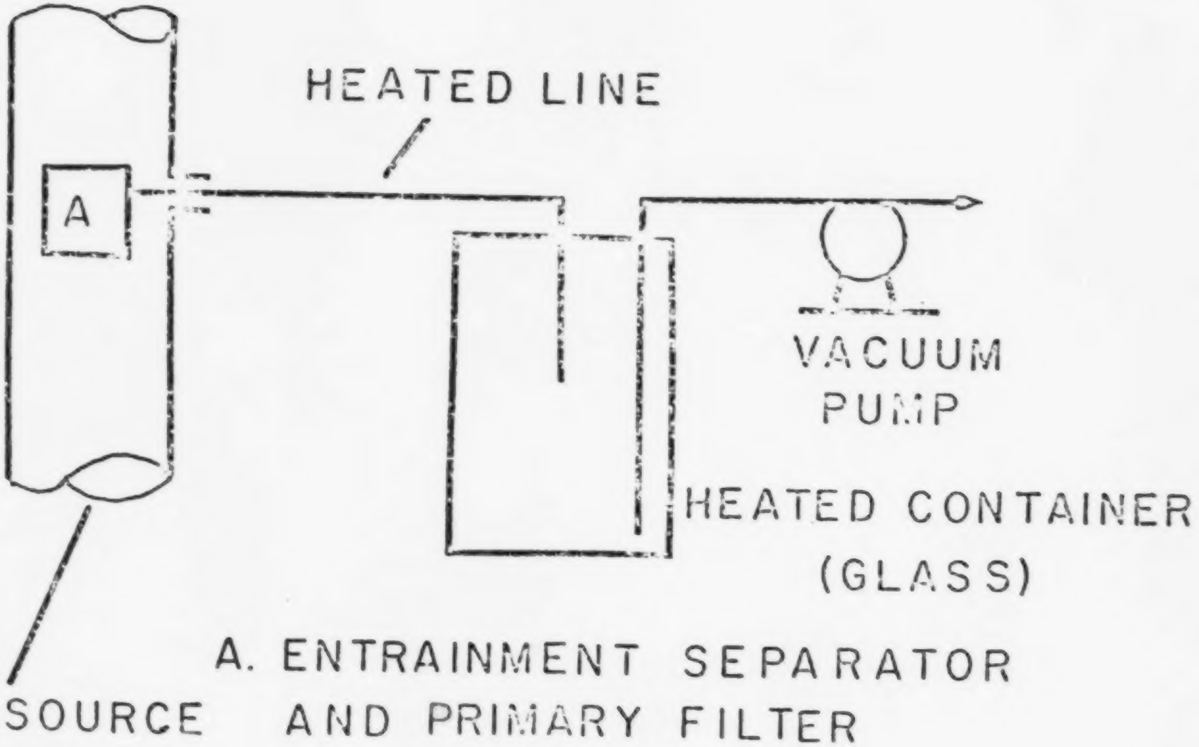
4.4.4 COLLECTION AND TRANSPORTING

Batch Systems - One commonly used method of batch sampling involves drawing a known vacuum on a heated container and subsequently drawing a sample from the source into the heated container until a pressure equilibrium is established. This technique has major disadvantages. Care must be taken to assure that collection lines are well purged to assure collection of a representative sample. Maintaining the gas temperature above the dew point when subsequently transferring to a multiport sampling valve is difficult. If the gas temperature is permitted to drop, dilution of the sample may occur as pressure is equalized. Displacement with an inert gas line leading to the bottom of the container is the common means of forcing the sample to a multiport sampling valve. This may result in some dilution. A simple procedure minimizes these problems by drawing a sample through an adequate probe, a heated sample line, and heated sample container. This permits purging of the sample container, line and probe, as well as allowing the walls of the sample container to reach equilibrium with the gas components present. Such a system is diagrammed in Figure 4-16.

The sample collection container is normally a glass burette fitted with Teflon stopcocks (stopcock grease reacts with most sulfur compounds) although any glass container can be used. Either must be equipped with a heating mantle. It is necessary to heat the container prior to its use and heating while collecting the sample to avoid any condensation is also required.

The temperature of the heated sample is maintained above the dew point prior to injection into the chromatograph. Transfer of the sample is by drawing or forcing a portion of the sample in the container into a multiport sample injection valve with care taken to insure the sample is maintained above its dew point at all times. Enough sample should be drawn through the valve to replace all gas in the sample loop and transfer line and yet not allow the significant dilution by the incoming inert gas or ambient air in the heated

FIGURE 4-16 BATCH SAMPLING SYSTEM


HEATED LINE
A
VACUUM
PUMP
HEATED CONTAINER
(GLASS)
A. ENTRAINMENT SEPARATOR
AND PRIMARY FILTER
SOURCE

container. The multiport sampling valve can be heated in an enlarged injector oven of the gas chromatograph or in a separate oven. It is not recommended that this valve be placed in the column oven as temperature can be varied at this location and can affect the performance of most commercially available valves.

Transfer of the sample from the sample container to the chromatograph injection port can be accomplished by syringe. A septum is placed on one port of the container, both stopcocks opened and at least one syringe of gas (more if required to evacuate any dead spaces) is removed and wasted to condition the syringe. The procedure is subject to some error due to the condensation that occurs in the syringe and remains in the needle, as well as the dilution that occurs as either ambient air or an inert gas replaces the sample taken from the sample container. This dilution is minimal and probably negligible if displacement gas is introduced opposite the point of withdrawal and care is used in rapidly transferring a minimum of sample volume.

Continuous Sampling Systems - Continuous sampling with the gas chromatograph may be performed by continuously drawing a conditioned sample from the desired source through a heated inert line attached to a multiport sampling valve. Injection of a sample into the column then consists of operating the sample valve on a routine basis. Electrically or steam heated Teflon sample lines are available commercially (1, 2, 3). The system used must include provisions for removal of particulate matter and entrained liquid as previously discussed.

Movement of the sample through the continuous flow line and the sampling valve must be accomplished with an air or water aspirator, or a vacuum pump since no known suitable inert and leak-proof pump is known to be available at this time.

Multiport sampling valves are available in six, seven, or eight-port models constructed of Teflon or 316-stainless steel or other suitable inert material (1, 2, 3). The use of Viton and other rubber or synthetic materials should be avoided since reduced sulfur gases can become adsorbed on the material, alter the gas composition, as well as cause mechanical malfunctions of the valve. Provisions for leak detection in systems operated under a vacuum must be made. Leaks are checked by isolating the complete system or sections thereof and placing them under negative head. The vacuum can be monitored with a manometer or gauge. A leak would be indicated by loss of vacuum.

The high sensitivity of the flame photometric detector (FPD) which results in non-linear detector response above a sulfur concentration of about 5 ppm (v/v) either required dilution of the sample or equipment modifications which permit analysis of samples containing well above 5 ppm concentrations. Stevens et al (3) describe a dilution system used in conjunction with the FPD for continuous analyses of source gases. While the system is complex it has functioned well in special study application. A drawback of the system is the use of at least three pumps whose short term performance casts some doubt on long term performance capability in routine monitoring situations. MC/SI has constructed and used a dilution apparatus in continuous flow special studies of source emissions. In this system a previously filtered source gas is maintained at a temperature above the dew point. After fine filtration for further particulate reduction, a known volume of source gas is mixed with a known volume of inert gas such as nitrogen. Flows of gas are measured with rotameters calibrated under the pressure and temperature conditions of use (e.g. 190 to 200°F, negative and positive head) and flow rate controlled with micrometering valves. A commercial dilution device to be used in continuous monitoring applications in conjunction with their FPD is currently marketed by Meloy Laboratories, Inc., Springfield, Virginia.

4.5 ELECTROLYTIC TITRATION OF SULFUR COMPOUNDS

An electrolytic titrator which is commercially available has found fairly widespread use in the kraft wood pulping industry, particularly in the more modern installations. This analytical system is most commonly referred to as a Barton titrator and is commercially available from the Barton Instrument Company, a division of International Telephone and Telegraph Corporation. The system, as currently marketed, has direct application to the continuous monitoring of recovery furnace gases However, with some modifications, described herein, the titrator is adaptable to most major gaseous sulfur emissions in the kraft pulp mill.

The concentration of the reactive compounds may be expressed in terms of the amount of known reagent added. In the Electrolytic Titrator, the gas sample continuously passes through the titration cell at a constant flow rate. The reagent for sulfur compounds is bromine, which is generated by an electrical current passing through the cell solution. The amount of current supplied to the cell is automatically adjusted by the solid-state circuit in the control module. The current provided by the control module produces just enough bromine to satisfy the demand of the reactive compounds in the sample and thus continuously maintain the end-point condition. The amount of current required to maintain the end-point condition is proportional to the concentration of reactive compounds in the sample (2).

The main functional components of the titration cell consist of a set of three electrodes arranged to form two functional pairs. One pair acts as the bromine-generating electrodes and the other pair serves as the sensing and control electrodes. The anode is common to both pairs of electrodes. Changes in the bromine level of the cell electrolyte cause the sensing electrodes to vary the current supplied to the input of the electronic circuit in the control module. As a result of the action of the sensing electrodes and the electronic circuit, current is allowed to pass through the generating pair of electrodes only when the bromine level in the cell falls below the preset operating bromine level ("blank" level). The current is proportional to the TRS present in the sample.

All compounds oxidizable by bromine will contribute to the bromine demand as the sample passes through the cell. The various organic and inorganic sulfur compounds react according to their chemical nature.

Sulfur combined in the form of mercaptans or organic sulfide does not require the same smount of bromine for reaction as sulfur combined as hydrogen sulfide. Furthermore, one compound can react according to two or more patterns. In a very low concentration range, the reproducibility of the bromine oxidation reactions is reliable to about ± 10% over reasonable periods of operation on a given sample source. For a specifically accurate sulfur measurement, it is necessary to titrate compounds each as H_2S, RSH, and RSR separately and apply an appropriate factor to the titration current required for each. The total then would equal the total sulfur concentration. This can be done by manual or automatic filtration using a scrubber solution selective to the compound in the sample stream. Usually, the total of TRS is expressed as equivalent H_2S.

The decrease in titration current that occurs when the compound is removed in the scrubber solution is a measure of its concentration. In most applications, however, the selective filter system is not required, since it is necessary to know only the variation in the total bromine generated for all compounds present. The instrument may be used as a continuous monitor on wet gas streams providing the moisture in the gas stream is reduced to the dew point at ambient conditions and the bulk of the particulate material is removed before the gas enters the cell. The system is normally operated to determine the total reduced sulfur concentration (minus SO_2) with the manual selecte scrubber-filter system to establish the concentration of individual components.

Figure 4-17 depicts a system which has functioned well at sources such as the kraft recovery boiler, kraft recovery stack, and smelt tank vents. The system consists of (a) a probe which is packed with glass wool for use where particulate concentration is high, (b) a reservoir for storing 5 percent potassium biphtalate, (c) an orifice which restricts flow of biphthalate solution to 0.5 to 1 ml minute, (d) a scrubber which removes particulate and SO_2 and cools the gas stream to ambient temperatures, (e) the necessary tubing to conduct the scrubbed gas sample to the cell, and (f) the pump, filter rack and other equipment used in batch sampling.

Figure 4-18 presents a modified sampling system which may be utilized as a continuous monitor on the recovery complex as well as other reduced sulfur sources in pulp mills. The substantial difference in the two transmittal and sensing systems shown is the thermal oxidation furnace preceding the titration cell. The function of the furnace is to oxidize the remaining sulfur gases, subsequent to the SO_2 scrubber to sulfur dioxide. This accomplishes two major objectives. The reduced sulfur compounds are all oxidized to SO_2 and sensed as SO_2 thus minimizing the calibrations which would be necessary for the individual compounds and also eliminates the possibility of "interference" from other non-sulfur bearing organic conponents .

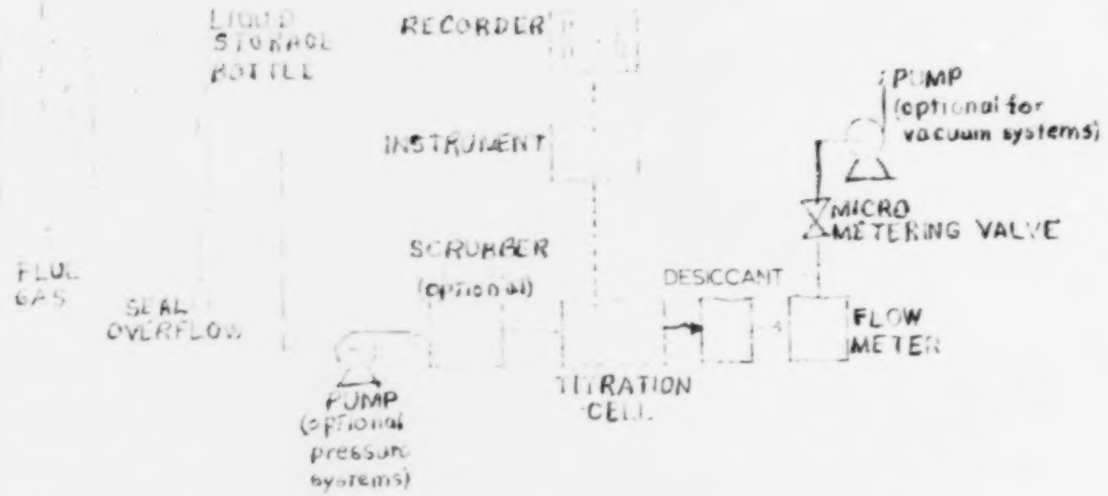

LIQUID STORAGE BOTTLE
RECORDER
INSTRUMENT
PUMP (optional for vacuum systems)
MICRO METERING VALVE
SCRUBBER (optional)
FLUE GAS
SEAL OVERFLOW
DESICCANT
FLOW METER
TITRATION CELL
PUMP (optional pressure systems)

FIGURE 4-17

CONTINUOUS SAMPLING SYSTEM

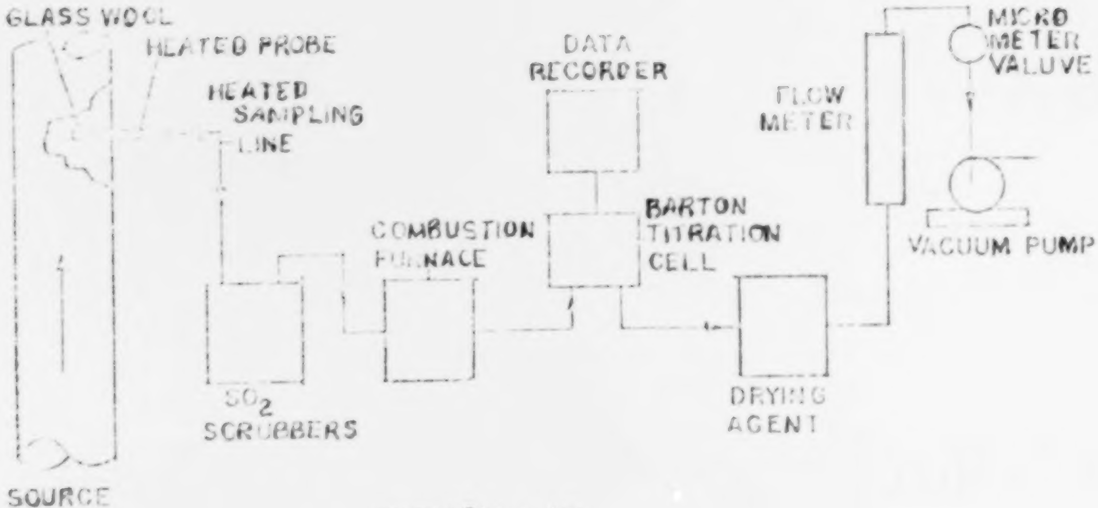

GLASS WOOL
HEATED PROBE
HEATED SAMPLING LINE
DATA RECORDER
FLOW METER
MICRO METER VALUVE
BARTON TITRATION CELL
COMBUSTION FURNACE
VACUUM PUMP
SO_2 SCRUBBERS
DRYING AGENT
SOURCE

FIGURE 4-18

BARTON SAMPLING SYSTEM

4.6 PARTICULATE MONITORS

Continuous particulate sampling and detection systems are currently receiving more attention and utilization in the wood pulping industry. To date, although not in widespread use, extractive and in-situ methods have been employed with varying degrees of success on wood pulping process units. The following sections describe those systems which have been used to continuously monitor particulates from such operations as kraft recovery furnaces, smelt dissolving tank vents, and lime kiln scrubber exhaust gases. As previously mentioned, the particulate material from these sources mainly consists of sodium sulfate, sodium oxide, calcium carbonate, and calcium oxide.

4.6.1 BOLOMETER-IN-SITU MONITOR

A light absorption device, the bolometer, used for many years in measuring smoke density has been found applicable for measurement of particulate loadings in kraft mill recovery furnace stack emissions. Calibration techniques involving wet test methods have shown that the instrument output signal has a semi-logarithmic relationship to particulate concentrations (6).

The bolometer utilizes a light absorption principle in continuously measuring the concentration of particulate matter passing a given point in the kraft mill recovery furnace flue gas system. The bolometer instrument consists of a light source and a detector head mounted on the opposite ends of a gas sample pipe or tube. The gas sample tube is commonly a length of standard 4-inch pipe with a 5-foot by 3 1/4-inch longitudinal slot cut on both sides of the pipe. This slot is normally centered in a horizontal or a vertical section of the ductwork or the stack being monitored. The light source is projected through the dust laden gases passing through the slot. The filament of the detector head is connected to a Wheatstone bridge measuring circuit. Changes in the dust loading or the dust density result in changes in the electrical resistance of the filament. A servo motor and measuring slide wire resistor maintain the Wheatstone bridge circuit balance and provide the instrument readout on the recorder. Normal instrument readout supplied by the vendor is from 0 to 100 percent of full scale (6).

As supplied from the vendor, the bolometer can be used for the measurement of dust density or smoke density. If the first measurement is desired, the instrument can be calibrated in either of the two commonly used units of dust loading measurement--grains per standard cubic foot of dry gas or grains per actual cubic foot of gas. If smoke density is the desired measurement, as is sometimes the case on power and/or combustion boilers, the problem of accurate Ringelmann Number determination is not encountered (5).

Figure 4-19 depicts the bolometer with a dial readout in a typical installation. Most of these instruments are installed with a recorded output on the control panel of the unit process in order that a continuous and permanent record of the operation may be accomplished. The continuous measuring aspects of this instrument enable optimization of operating variables which normally result in minimizing particulate emission levels. Malfunction of control devices (i.e., electrostatic precipitators) are rapidly detected which results in an economic saving of reusable chemicals.

4.6.2 CONDUCTIVITY (EXTRACTIVE) MONITOR

This monitor, Figure 4-20 uses a twin tubed sample probe to provide a non plugging sample line through which a flue gas sample is drawn. Water is continuously metered down one line of the sample probe to a point just back of the sample probe tip where it joins the second line which is carrying the gas away from the probe inlet. The water is sheared off by the gas flow and mixed with it until it reaches a separation-mixing tank. By the time the gas leaves this chamber it has left most of its heat and almost all of its dust load in the water. The water runs down an overflow tube to a water cooler and then to a conductivity cell connected to a continuous recorder. The conductivity is measured and is related to the sodium content of the water solution. A gas meter measures the gas drawn off the separation tank by a vacuum system.

With the water flow, gas flow and conductivity, i.e. sodium concentration, all known the sodium concentration in the flue gas is found by:

$$\text{sodium flue gas} = \frac{\text{water flow} \times \text{sodium concentration}}{\text{sample gas flow}}$$

To determine the total losses with the flue gas it is also necessary to know the volume of flue gas flow. The sodium losses are simply the flue gas flow times its concentration.

Although just out of the experimental stage, the monitor provides a continuous record of sodium losses with recovery flue gases. The principle of using a twin tube wet tip probe may be applicable to several other tests. By passing a solution of cadmium chloride through the tip and measuring the resulting turbidity of the final solution the amount of H_2S in the flue gas may be determined. If a fuschin solution were used in place of water and the color monitored, the amount of SO_2 in the stack gas might be determined.

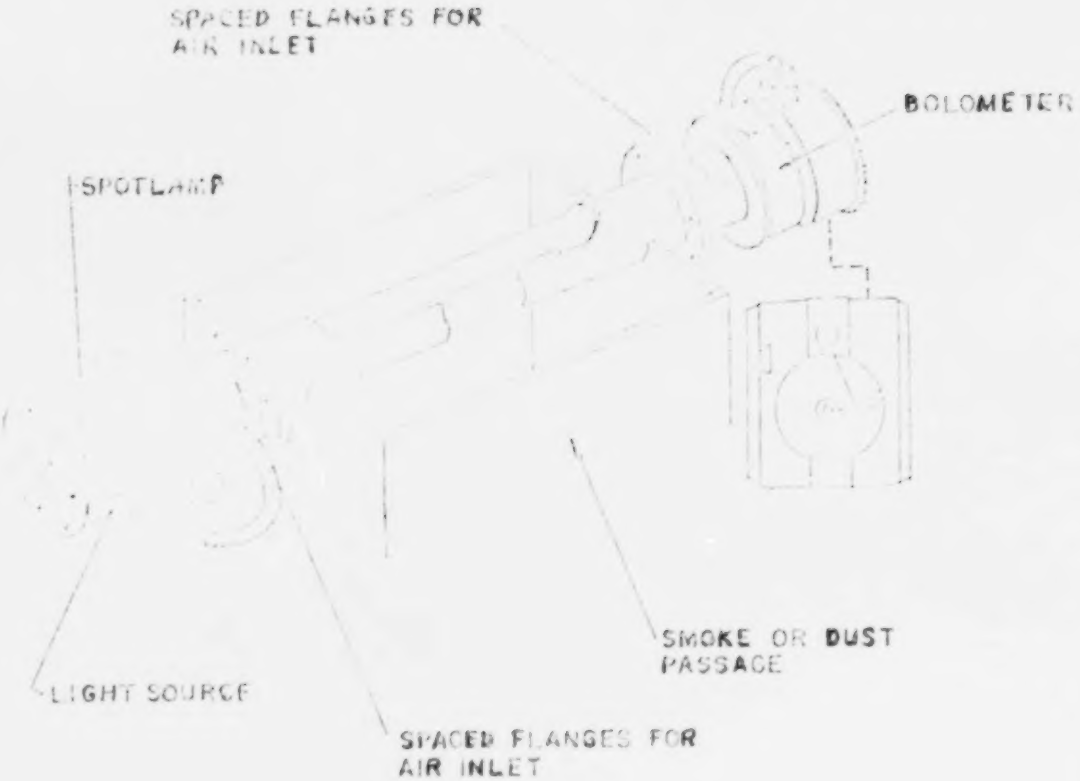

SPACED FLANGES FOR AIR INLET
BOLOMETER
SPOTLAMP
SMOKE OR DUST PASSAGE
LIGHT SOURCE
SPACED FLANGES FOR AIR INLET

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FIGURE 4-19 - Bolometer for Measurement of Particulate Emissions

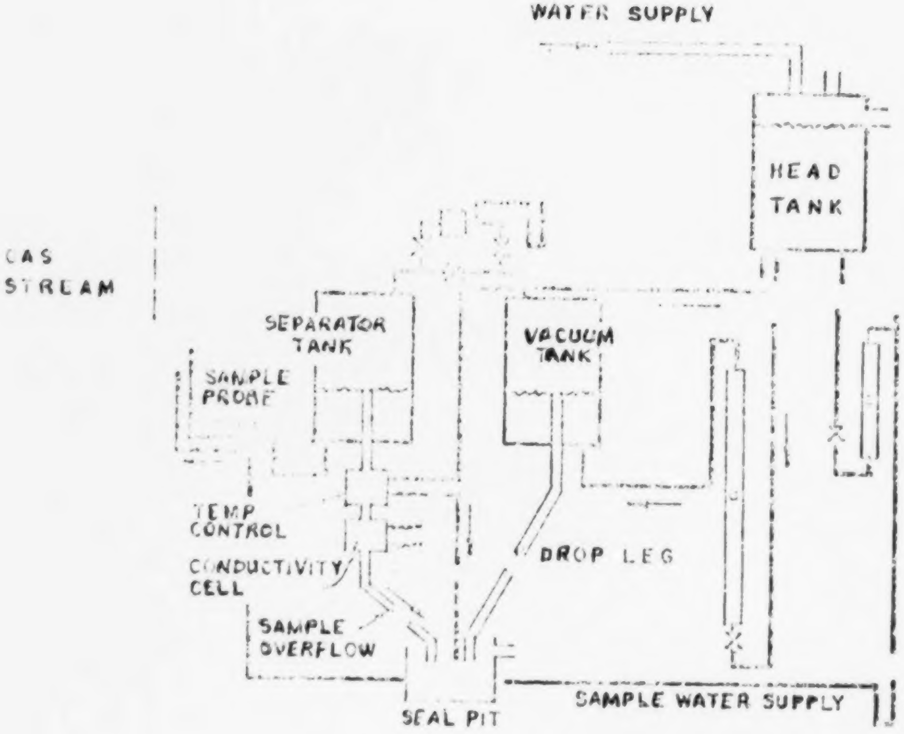
WATER SUPPLY
HEAD TANK
GAS STREAM
SEPARATOR TANK
VACUUM TANK
SAMPLE PROBE
TEMP CONTROL
CONDUCTIVITY CELL
DROP LEG
SAMPLE OVERFLOW
SEAL PIT
SAMPLE WATER SUPPLY

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FIGURE 4 - 20 - Titrimetric Instrument for Measuring Particulate Emissions

4.6.3 SPECIFIC ION (EXTRACTIVE) MONITORS

At least one kraft mill has experimented with a specific ion electrode method to continuously monitor particulate emissions from the recovery furnace complex.

Briefly the system employs a transmittal system which extracts particulate material from the exhaust gases at or near a previously determined, by conventional methods, isokinetic rate. The sample stream then enters a sensing cell equipped with a sodium ion electrode. The sodium ion concentration thus sensed is then translated and read out as sodium sulfate concentration. As stated, this method, although appearing to have application to wood pulping unit processes, has not found wide acceptance and, therefore, must be considered as still in the applied research and development stage.

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C H A P T E R 5

AIR POLLUTION CONTROL SYSTEMS

5.1 INTRODUCTION

Control methods presently in use in the wood pulping industry consist of add-on hardware or process modifications. The methods considered in this section are those which have been in reasonably successful operation for at least one year at one or more locations. Control methods are briefly described in general terms and are evaluated under conditions of specific applications. The evaluations include an effectiveness study as well as a discussion of engineering factors which are unique to the application.

A variety of methods is found to be useful in controlling particulate emissions from pulp mill sources. Efficiencies of 99+% are possible. The listing which follows identifies those methods most commonly used. It should be noted that the direct contact evaporator following the kraft recovery furnace is an important particulate control device. It should also be noted that where primary or secondary wet scrubbers are used as particulate collectors on combustion sources, the emission of gaseous sulfur compounds may be increased or decreased depending on the nature of the scrubber medium.

Kraft Recovery Furnace	- Electrostatic Precipitators - Venturi Evaporator/Scrubbers - Electrostatic Precipitators plus Secondary Scrubber
Kraft Lime Kiln	- Venturi Scrubber - Cyclonic Scrubber - Impingement Baffle Scrubber - Electrostatic Precipitators (recently)
Kraft Smelt Dissolving Tank	- Mesh Pads - Packed Tower Scrubbers - Orifice Scrubbers
Kraft Lime Slaker	- Mesh Pads - Cyclonic Scrubbers
Power Boilers	- Mechanical Collectors - Electrostatic Precipitators

Combination Boilers - Mechanical Collectors
Cyclonic Scrubbers

Fewer numbers of methods are in use for the control of gaseous emissions, particularly the odorous reduced sulfur compounds. The majority of odorous emissions can be grouped into three categories: (a) recovery furnace offgases; (b) low volume high concentration sources such as the noncondensible gases from the multiple effect evaporators, and digester relief and blow gases; (c) high volume low concentration sources such as brown stock washers and smelt dissolving tanks. Wet scrubbers have received limited application on combustion sources in the kraft process because of the difficulty of absorbing effectively all of the odorous compounds with a single scrubbing medium. Also as indicated previously, the emission of gaseous sulfur compounds may be increased or decreased depending on the nature of the scrubbing medium. The following list identifies those methods most commonly used and which are described in the chapter:

Kraft Recovery Furnace - Weak Black Liquor Oxidation
- Strong Black Liquor Oxidation
- Proper Operation
- Venturi Evaporator/Scrubber
- Cyclone Evaporator/Scrubber
- New Recovery System Design

Kraft Smelt Dissolving Tank - Packed Tower Scrubber
- Orifice Scrubber

Kraft Digester Relief and Blow plus M.E. Evaporator - Chlorination
- Incineration
- Packed Tower Scrubbers
- Weak Black Liquor Oxidation (M.E. Evaporators)
- Steam Stripping of Condensates
- Air Stripping of Condensates

Sulfite Acid Tower - Additional Absorption Tower

Sulfite Blow Pit - Packed Tower

5.2 GENERAL DESCRIPTION OF CONTROL EQUIPMENT

5.2.1 ELECTROSTATIC PRECIPITATORS

An electrostatic precipitator consists in principle of a number of discharge (emitting) electrodes, collecting electrode plates and a high-voltage power unit. This power unit comprises high-voltage transformers and rectifiers to convert the available AC power to high-voltage DC power. Lately, silicon diode rectifiers have almost exclusively replaced other types of rectifiers.

The dust laden gas enters the electrostatic precipitator and flows in the passages created by the collecting electrodes. When high-voltage power is applied to the discharge electrodes located in the passages, ionization or corona discharge occurs near the surface of the discharge electrodes. The negative ions attach themselves to dust particles near the electrodes giving the particles a negative electric charge. The charged dust particles are repelled by the discharge and attracted to the collecting surfaces connected to ground. Here the dust particles lose their electrical charge and are deposited on the collecting electrodes.

The collecting electrodes are provided with a rapping mechanism for dislodging the dust precipitated on the electrodes. This rapid system must be designed very carefully to avoid creation of a dust cloud in the space between the electrodes. Incorrect rapping operation or programming may cause the dust to re-entrain which, in turn, would greatly decrease the dust collecting efficiency of the precipitator. Incorrect rapping is the most common cause for so-called "snow-outs." The rapping mechanism, which is generally operated on an automatic time cycle basis, is either of vibrator or motor driven fall-hammer type. Vibrators are preferred for pulp mill applications rather than the hammer rappers which are used more frequently, for example, on fly ash precipitators.

The high voltage power level is controlled by an automatic control unit. The discharge electrodes are connected to the negative rather than to the positive side of the power supply. A higher voltage can thereby be maintained without excessive arc-overs which, in turn, would cause waste of electric power and eventually lead to operating difficulties. The automatic voltage rate of sparking provides a feedback to the control unit making it possible automatically to operate the electric system of the precipitator at optimum conditions. Little or no sparking will increase the voltage and too much sparking will reduce the voltage, thereby preventing arc-overs detrimental to the precipitator.

Gas conditions are never uniform throughout the precipitator. Aside from unintended irregularities in gas distribution and other conditions, the dust loading varies from inlet to outlet of the precipitator. To reach optimum dust collecting efficiencies, the electrical control units must accomodate these variations. A high dust loading will increase the sparking and reduce the voltage. If the precipitator would have only one electric system with one automatic voltage control, the voltage throughout the precipitator would be limited to the lowest voltage permissible at any point in the precipitator. The modern precipitator is, therefore, divided into independent electrical units, each controlled for maximum voltage depending on the gas conditions in that particular section of the precipitator. The discharge system close to the outlet of the precipitator will consequently operate at a higher voltage level than the inlet. This need for sectionalizing has led to increased use of the horizontal flow, plate-type precipitator. This type has superseded the tube-type, vertical flow precipitator, once very common in the pulp and paper industry. The tube-type precipitator does not easily lend itself to sectionalizing.

The electric power consumption of a precipitator depends on several factors. The input of current is necessary to sustain the voltage level. There is a constant power drain due to ionization in the corona, due to the controlled sparking and other voltage leakages because of poor maintenance, dust build-up, et cetera. The collection efficiency depends on the voltage level; but, on the other hand, the higher the voltage level, the greater the power drain. At 90 percent collection efficiency, the power consumption is approximately 0.2 kw/1000 CFM of gas and at 99.9 percent efficiency, the power consumption has risen to approximately 0.8 kw/1000 CFM.

Most precipitators used in the wood pulping industry on recovery boilers are designed for collection efficiencies of 90 - 99.9 percent. The pressure drop of the gas passing through the precipitator is usually below 0.5 inch W.G. A typical wet-bottom precipitator with tile shell is shown in Figure 5-1.

5.2.2 VENTURI SCRUBBERS

The Venturi scrubber consists in principle of a convergent section (throat) and a divergent section. Dust laden gas enters the convergent section and is accelerated to high velocity as it approaches the throat. Gas velocities in the throat section vary from 100 to 500 FPS.

Water or other scrubbing liquid is injected either directly into the throat section or the top of the Venturi. In the latter case, the scrubbing liquid cascades down the walls of the convergent section. The high velocity gas stream atomized the liquod into a fine mist--the greater the velocity, the finer the droplets. Collison between the dust particles and the water droplets takes place and causes the dust to be entrapped in the water. Further collison between the water droplets occurs. This will create aggregate droplets of relatively large size. These droplets are easily separated from the gas stream in a subsequent separator. The collision or impaction phenomenon is rather complex, but is mainly due to mass forces created by the great velocity differential between the dust particles and the water droplets. For submicron particles, the Brownian molecular movement, diffusion, and electrostatic forces also play an important role.

In the divergent section, the gas and the dust particles are decelerated thereby creating a new velocity differential with additional agglomeration. Finally, in the elbow connecting the Venturi and the separator, as well

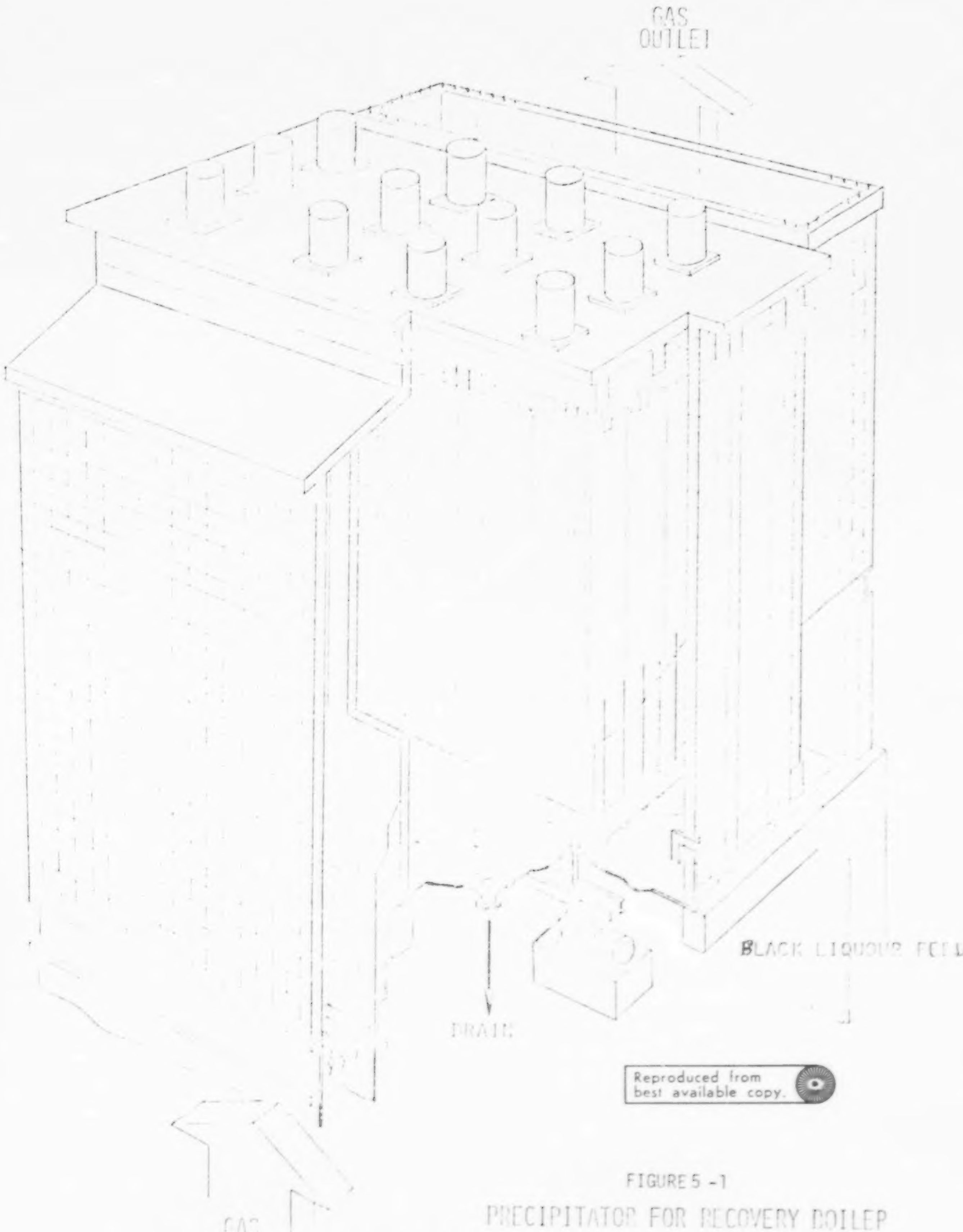
GAS OUTLET
BLACK LIQUOUR FEED
DRAIN
GAS INLET

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FIGURE 5 -1

PRECIPITATOR FOR RECOVERY BOILER

as in the inlet to the separator (if radial), changes of direction of the gas flow cause additional impaction and agglomeration.

The gas and liquid enter the separator, usually of the cyclonic type, where the liquid is thrown to the walls by centrifugal forces and drains to the bottom by gravity. The clean gas exists through the upper portion of the separator.

The elbow connecting the Venturi with the separator is either of the regular type or of so-called flooded types. The flooded elbow is developed to prevent erosion. Here the liquid surface absorbs the brunt of the water and dust stream. For pulp mill applications, such as lime kiln scrubbers, the flooded elbow is recommended.

Normally the separator is of the cyclonic type with conical bottom and either top outlet or side outlet. The type of outlet depends on whether the fan is located before or after the scrubber. The top outlet lends itself to a direct mounted stack. In order to facilitate the installation, the separator is sometimes provided with a flat bottom. This may sometimes create drainage problems. For special purposes a so-called false bottom is also installed. The false bottom creates an intermediate reserve for the scrubbing liquid where de-aeration can take place making the scrubbing liquid (e.g., black liquor) more suitable to pump. Scrubbers for recovery boilers are almost always provided with facilities for wall wash of the separator. This prevents build-up of black liquor solids which can be a fire hazard, in addition to being a maintenance problem.

The Venturi scrubber is capable of high efficiency collection of dust and fumes even in the submicron range. The efficiency of collection is a function of the pressure drop across the scrubber which in turn is a function of the gas velocity in the throat and the liquid flow rate (liquid to gas ratio). The higher the gas velocity or the liquid flow rate, the greater will be the pressure drop and consequently the greater the efficiency. There is, however, a cut-off point where increased liquid flow rate will have an adverse effect on the collecting efficiency. The throat becomes "flooded." This occurs at about 20 gallons per 1000 CFM. In order to attain high collecting efficiency, the water droplet size distribution has to be in a certain relation to the dust particle size distribution. Too large droplets would reduce the probability of collection drastically, and even if collection would take place the chance for the dust particles to be entrapped in water would also be reduced.

Increased gas velocity (pressure drop) increases the atomization. A fine dust will, therefore, require a higher pressure drop than a coarse dust for the same collecting efficiency.

Scrubbing liquid is injected into the Venturi at low pressure through relatively large jets or open weirs. In order to be able to recirculate the scrubbing liquid, in other words maintain a high concentration of solids, the manufacturers try to completely do away with narrow constrictions and weirs. The liquid rate is normally 3 - 15 gallons per 1000 CFM of gas. A typical Venturi scrubber is shown in Figure 5-2.

5.2.3 CYCLONIC SCRUBBERS

The cyclonic scrubber is an efficient device for removing dust particles two microns and larger and is also a relatively good gas absorber. In this unit, the dust laden gas enters tangentially at the bottom of a cylindrical tower and spirals upward through the scrubber in a continuously rotating path. A spray manifold is located axially in the center of the scrubber with banks of spray nozzles directed radially toward the walls. The spray sweeps across the path of the gas stream intercepting and entrapping the dust particles. The centrifugal motion of the spray impacted by the rotating gas causes the droplets to impinge against the walls of the scrubber and drain to the bottom due to gravitational forces.

In another type of cyclonic scrubber, the spray nozzles are mounted on the wall rather than in a central spray manifold. The advantage with this type is that the nozzles may easily be serviced or replaced while the scrubber is in operation.

The mechanism of collecting particles in the cyclonic scrubber is in essence the same as in a Venturi scrubber; namely, impaction and agglomeration of liquid droplets and dust particles with subsequent centrifugal and gravitational separation.

The liquid pressure ranges from 50 to 400 PSIG. The flow rate is normally 3 - 8 gallons per 1000 CFM.

The cyclonic scrubber is most efficient on relatively coarse dust and the efficiency drops off markedly for particles under two microns. The pressure drop is considerably less than for a Venturi scrubber and ranges normally from 0.5 to 3 inches WG. A typical cyclonic scrubber is shown in Figure 5-3.

5.2.4 IMPINGEMENT BAFFLE SCRUBBERS

The impingement baffle scrubber is a vertical tower equipped with one or more impingement baffle stages. The impingement baffle consists of a perforated plate having a multitude of small holes so arranged that a baffle is located directly above each perforation. A weir on each plate maintains a level of scrubbing liquid.

The contaminated gas enters radially at the bottom of the scrubber and is subjected to a water spray that will precipitate out the coarser dust particles. The gas then passes through the perforations and impinges

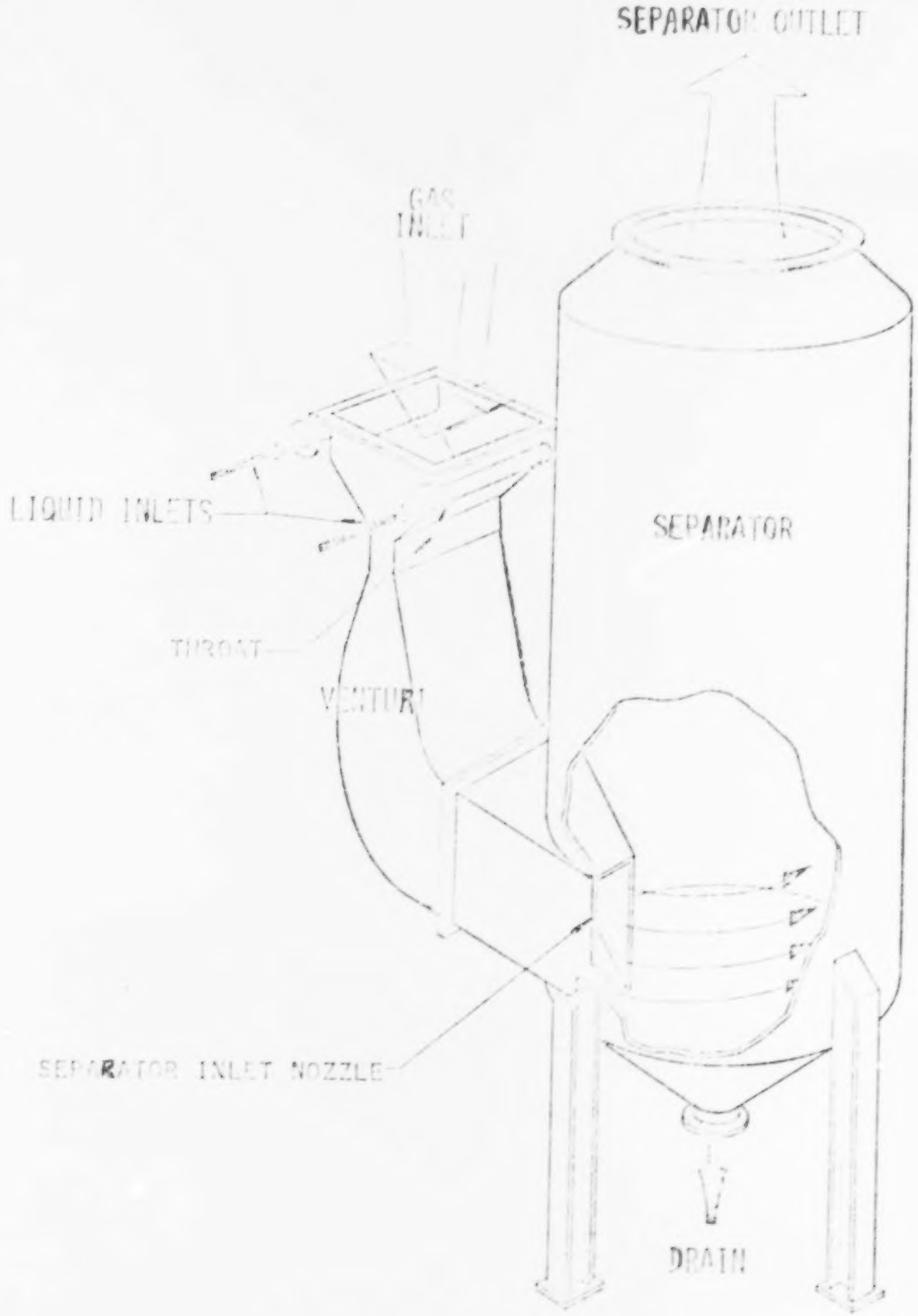

SEPARATOR OUTLET
GAS INLET
LIQUID INLETS
SEPARATOR
THROAT
VENTURI
SEPARATOR INLET NOZZLE
DRAIN

FIGURE 5-2

VENTURI SCRUBBER WITH CYCLONIC SEPARATOR

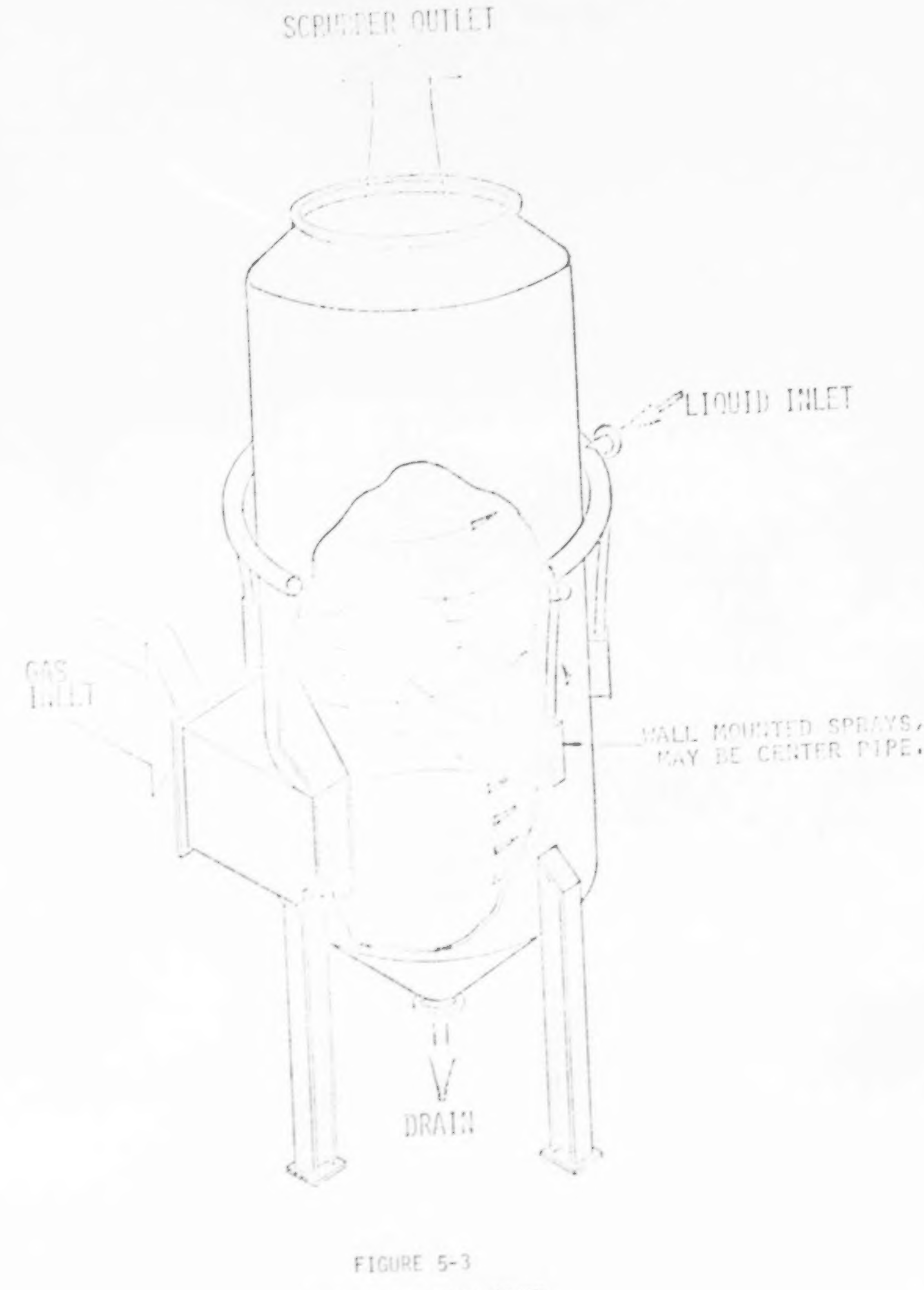

SCRUBBER OUTLET
LIQUID INLET
GAS INLET
WALL MOUNTED SPRAYS, MAY BE CENTER PIPE.
DRAIN

FIGURE 5-3

CYCLONIC SCRUBBER

on the baffles. The gas velocity through the perforations, ranging from 75 to 100 FPS, atomizes the scrubbing liquid and the velocity differential between gas and liquid results in the impaction and agglomeration of liquid and particulate matter. The scrubbing liquid is introduced into the scrubber through low pressure spray nozzles located below the plates and spraying upward. These sprays not only deliver liquid to the plates, but also serve to cool and humidify the gasses; remove coarse particles; and keep the bottom of the plates clean. For scrubbers with more than one stage, the scrubbing liquid is drained off the plates downward from stage to stage in the scrubber. In addition to the multiple impaction, the change of solids concentration in the liquid also contributes to increasing the collecting efficiency.

The pressure drop for impingement baffle scrubbers ranges from 2 inches WG to 8 inches WG depending on the number of stages, size, and numbers of perforations and baffles. As would be expected, increased number of stages and smaller perforations result in higher pressure drop and subsequent higher efficiency. An impingement baffle scrubber is shown in Figure 5-4.

The impingement baffle scrubbers are normally used in lime kiln applications. The efficiency is, however, not high enough to comply with today's air quality requirements. For upgrading of existing impingement baffle scrubbers, it is possible to install a Venturi and an elbow ahead of the scrubber and to use the scrubber shell as a cyclonic separator. The inlet to the scrubber must, in such a case, be changed to enter the shell tangentially, and all the internal parts have to be removed.

5.2.5 PACKED TOWER SCRUBBERS

The packed tower scrubber is used primarily as a gas absorber. Its use for collection of solid particulates is limited because it is rather inefficient for particles under five microns and is subject to becoming plugged because of dust build-up. It is, however, an excellent device for absorption of such gases as HCl, SO_2, Cl_2, H_2S, and NH_3. Other advantages of the scrubber are simple design and low manufacturing cost.

The scrubber consists of a vertical cylindrical shell with the gas inlet at the bottom and the outlet at the top. Above the gas entrance is a packed section consisting of four or more feet of packing material. This packing may consist of Raschig rings, Pall rings, saddles, et cetera, made from stoneware, ceramic, or polypropylene. Water is distributed uniformly over the packing by means of low pressure spray nozzles or weirs located above the packing. Normally, there is a mist eliminator above the spray nozzles to prevent entrainment of liquid in the clean gas leaving the tower. Normally a reservoir is located at the bottom of the scrubber for direct recirculation. A typical packed tower scrubber and packing are shown in Figure 5-5.

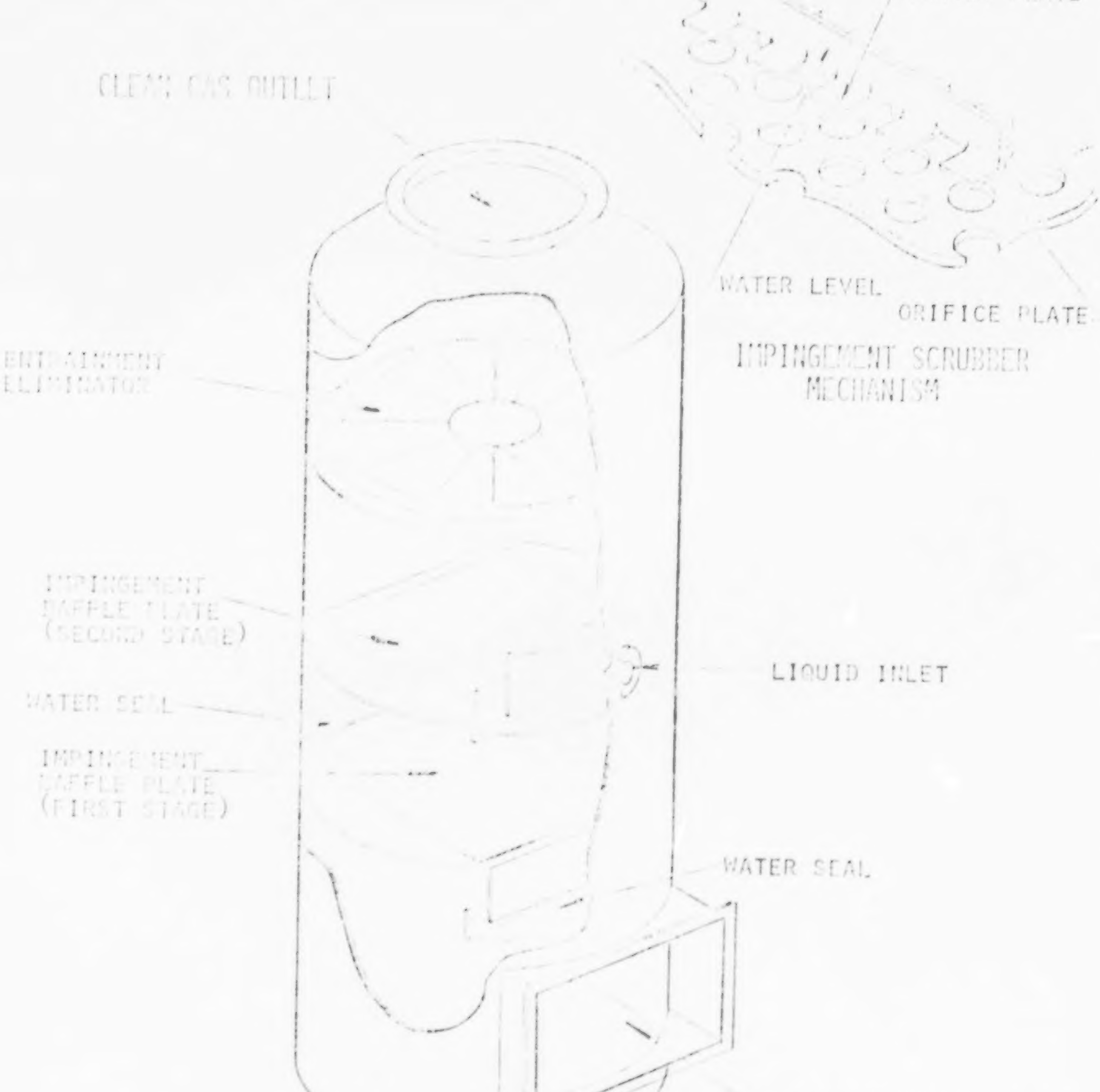
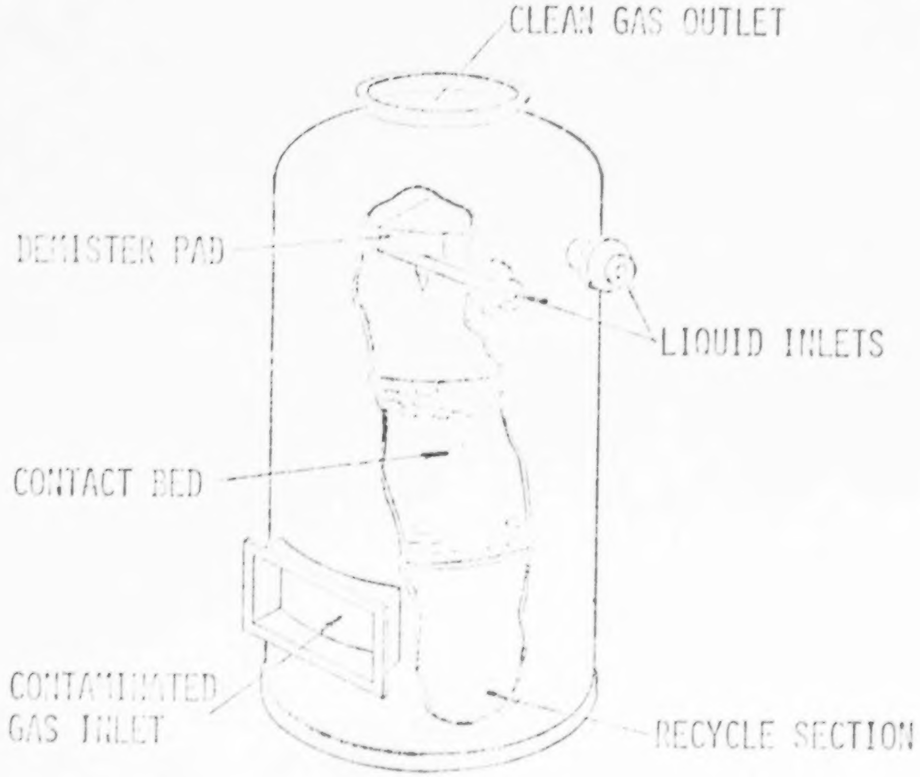
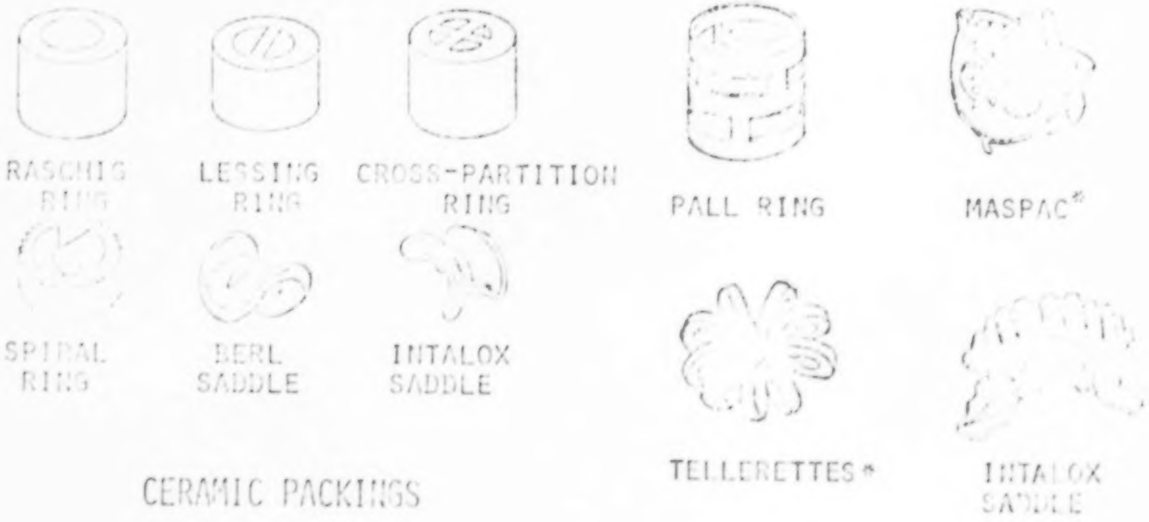

TARGET PLATE
CLEAN GAS OUTLET
WATER LEVEL
ORIFICE PLATE
IMPINGEMENT SCRUBBER MECHANISM
ENTRAINMENT ELIMINATOR
IMPINGEMENT BAFFLE PLATE (SECOND STAGE)
LIQUID INLET
WATER SEAL
IMPINGEMENT BAFFLE PLATE (FIRST STAGE)
WATER SEAL
CONTAMINATED GAS INLET
DRAIN

FIGURE 5-4

IMPINGEMENT SCRUBBER


CLEAN GAS OUTLET
DEMISTER PAD
LIQUID INLETS
CONTACT BED
CONTAMINATED GAS INLET
RECYCLE SECTION

COUNTER-FLOW PACKED TOWER SCRUBBER


RASCHIG RING
LESSING RING
CROSS-PARTITION RING
PALL RING
MASPAC®
SPIRAL RING
BERL SADDLE
INTALOX SADDLE
TELLERETTES®
INTALOX SADDLE

CERAMIC PACKINGS

PLASTIC PACKINGS

FIGURE 5-5

The contaminated gas enters at the bottom of the tower and moves upward through the packing counter-current to the scrubbing liquid. The packing forces the gas to follow a tortuous path over the contact surfaces and interstices creating intimate contact with the descending liquid.

The pressure drop over the tower depends on the height of packing but is normally in the order of 1 - 2 inches WG.

As mentioned before, the packed tower is an excellent gas absorber, but less suitable for dust removal due to dust build-up. When dust is present in the gas, special attention has to be given to the selection of packing material. A larger size packing; i.e., 4-inch Pall rings instead of 2-inch should be chosen in order to prevent plugging. The contact surface will thereby be reduced and the gas absorption efficiency will drop. This can be compensated for by increasing the height of the packing but the plugging tendencies will increase simultaneously.

5.2.6 MECHANICAL COLLECTORS

There are a great number of different mechanical collectors in use throughout industry. The most common ones within the wood pulping industry are the large diameter cyclones and the multi-tube collectors. This description will be limited to these two types.

Cyclone dust collectors are of cylindrical or conical type, utilizing centrifugal and gravitational forces for separation of dust particles from a gas stream. The dust laden gas enters the collector tangentially either directly or via an expanded involute section where the dust particles are subjected to the separating forces. The centrifugal force drives the dust particles to the collector wall; the gravitation drives the concentrated dust downward to the cone outlet; and the dust is discharged into a collection hopper while the cleaned gas flows upward in an inner vortex to the gas outlet tube.

Two basic types of cyclone collectors are available--the tangential inlet type shown in Figure 5-6 and 5-7 and the axial vane type. The former is sometimes referred to as large diameter cyclone, or cyclone collector, and the latter one as a tubular collector. In the tangential inlet type, the gas enters the cyclone through a straight tangential, helical, or involute inlet section. Axial vane units employ inlet vanes to provide the spiraling motion to the dust laden gas stream.

Many sizes and designs of cyclone collectors can be provided to meet specific dust collection problems. The units may be installed in single or multiple arrangements, in parallel or in series. Cyclone collectors are generally suitable for separating solid particles in size ranging from about 3 microns to 200 microns. They can, of course be used for larger particle sizes also.

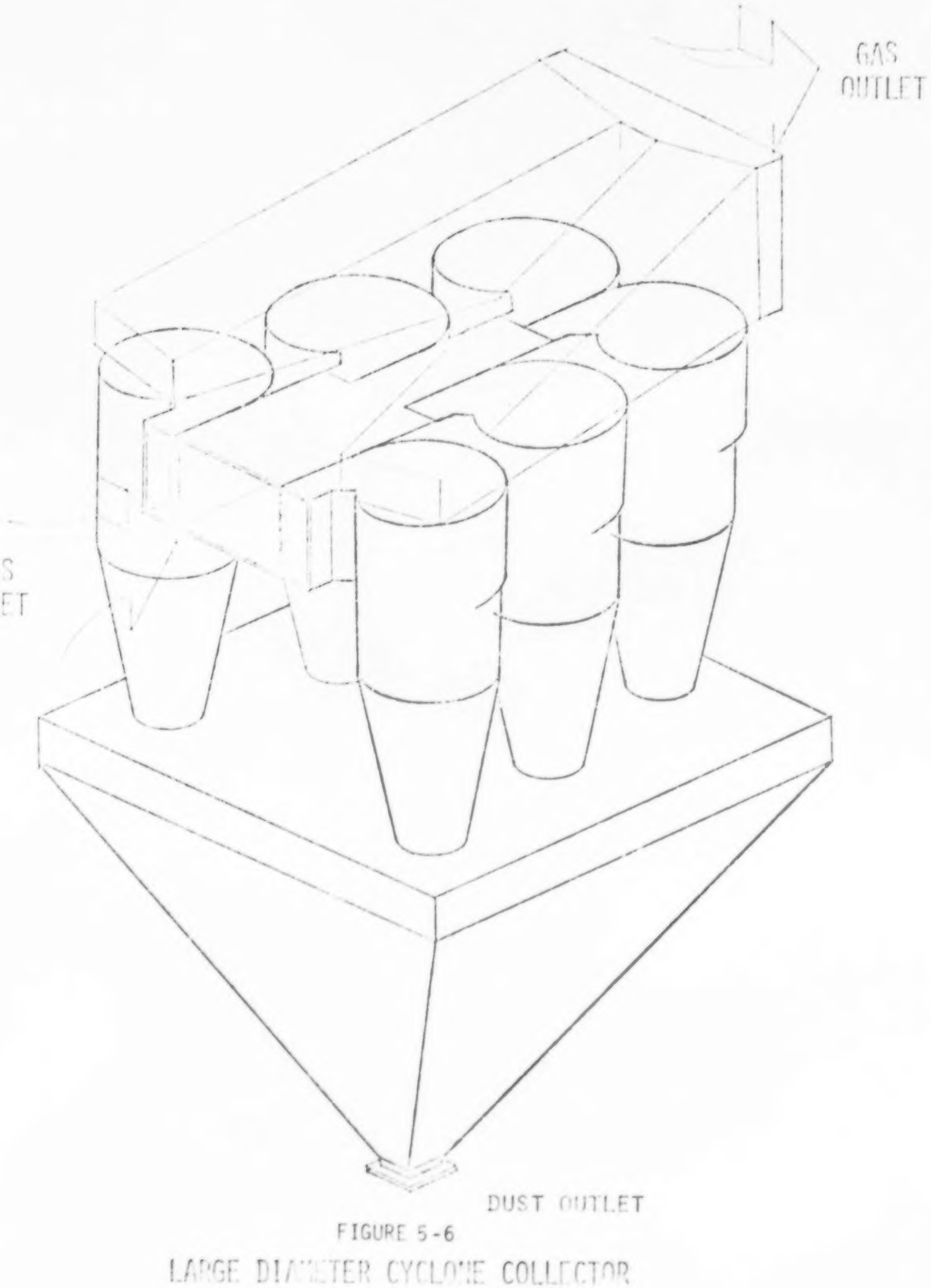
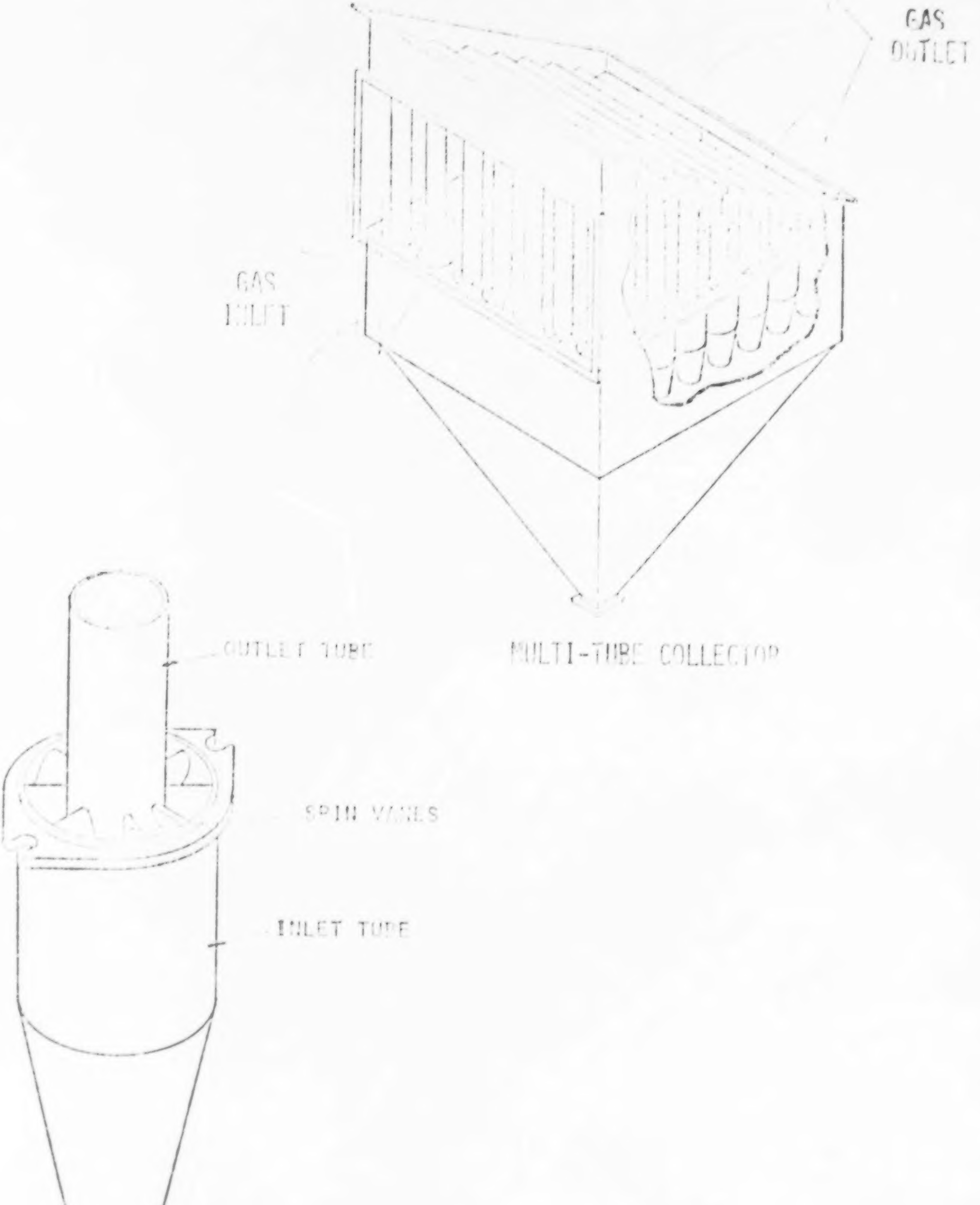

GAS OUTLET
GAS INLET
DUST OUTLET

FIGURE 5-6

LARGE DIAMETER CYCLONE COLLECTOR

STANDARD ARRANGEMENT


GAS OUTLET
GAS INLET
OUTLET TUBE
SPIN VANES
INLET TUBE

MULTI-TUBE COLLECTOR

COLLECTOR ELEMENT

FIGURE 5-7

For a given cyclone collector, the overall collecting efficiency can be determined if certain parameters are known. These parameters include dust particle size distribution, density, concentration, and other properties of the dust. Gas temperature, pressure, moisture content and gas composition, as well as pressure drop limitations and local conditions, are also factors of consideration. The efficiency increases with increased dust particle size, density, and concentrations. Collection efficiency increases with increased pressure drop across the cyclone. The collector can be designed for pressure drops of less than 2 inches WG for large diameter cyclones and for 2 - 7 inches WG for the smaller diameter (high efficiency) units.

Increasing temperature will decrease the efficiency of the cyclone. However, up to 700°F, the influence of the gas temperature is not great. For the same pressure drop, increased gas viscosity or density will lower the collecting efficiency.

As particle size, dust density, and inlet gas velocity decreases the efficiency tapers off. Overall efficiency of the collection system can be increased by arranging the cyclones in series. By reducing the diameter of the cyclone the centrifugal forces increase, thus increasing the efficiency. The gas volume capacity will, however, simultaneously be reduced and the number of cyclones has to be increased. This principle is utilized in the multi-tube collectors where the tube diameter is from 12 inches or less up to 24 inches. Batteries of tubes are mounted in the same casing and high efficiencies are attainable.

Since high efficiencies require high radial gas velocities, abrasion is often a problem for cyclone collectors. Proper selection of material of construction is imperative. Materials in use include carbon steel, low alloy steels, aluminum and special materials. Abrasion resistant linings in castable form or brick linings can also be used.

5.2.7 BLACK LIQUOR OXIDATION

Black liquor oxidation is practiced for the purpose of oxidizing the sodium sulfide in the liquor. This is accomplished by reacting the sodium sulfide with oxygen in the air to form sodium thiosulfate. This compound is relatively stable and will not break down in passing through the direct contact evaporator. Sodium sulfide reacting with the carbon dioxide and sulfur dioxide in the flue gases is the cause of hydrogen sulfide emissions. The chemical reactions of sodium sulfide (unoxidized liquor) and CO_2 and SO_2 in the flue gases are as follows:

$$Na_2S + CO_2 + H_2O \rightarrow Na_2\,CO_3 + H_2S$$

$$Na_2S + SO_2 + H_2O \rightarrow Na_2\,SO_3 + H_2S$$

Black liquor oxidation can be applied either to weak black liquor or to concentrated black liquor. The choice is dependent to a considerable extent on the characteristics of the liquor. Usually weak liquor oxidation is used on non-foaming liquor and concentrated liquor oxidation on foaming type liquor. Regardless of the type of oxidation, it is essential that complete oxidation of the sodium sulfide takes place, if hydrogen sulfide emissions from the direct contact evaporator are to be prevented.

Lately, investigations have been conducted into sodium sulfide reversion taking place after weak liquor oxidation. Instances are known to exist where, although there is 99 plus percent oxidation during weak liquor oxidation, the concentrated liquor shows the presence of sodium sulfide. One solution is to add a second system of concentrated liquor oxidation. Among those who have installed weak liquor oxidation and who are having sodium sulfide reversion, there are suggestions that concentrated liquor oxidation might be the correct installation (14).

There are three types of oxidation systems:

1. Packed Towers
2. Bubble Tray Towers
3. Air Sparged Reactors

Packed Towers

Packed towers have been applied primarily to weak black liquor oxidation. The principal advantage of a packed tower lies in reduced power costs. The pressure drop through a packed unit is usually about 1 to 2 inches WG, and a tower for a 500 ton-per-day mill will require about 20 hp to operate the required air blowers. In regions of high power costs, this is an important factor in selecting an oxidation unit. The disadvantage of this unit is that it has plugging tendencies and has lower oxidation efficiency.

Bubble Tray Towers

The bubble tray oxidation tower is used for weak black liquor oxidation only. The liquor is pumped out on a perforated steel plate, under which air is blown from a fan. The air passes through the perforations and bubbles through the liquor. The liquor height on the plate is normally four to six inches and the liquor makes several passes over the plate. In order to accomodate larger flows of liquor, a number of these aeration chambers (bubble trays) are connected in parallel and stacked on top of each other.

The liquor, air, and foam are discharged into a foam tank, where mechanical foam breakers convert the foam to liquor. Certain liquors with low foam characteristics may not require foam breakers if the tank is large enough. The air leaving the system through foam breakers carries some entrained liquor. This liquor is separated from the air in a cyclone and returned to the foam tank, while the air is exhausted to the atmosphere. This air stream, although relatively small, contains some hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide.

The system operates at 25 - 35 inches WG pressure drop. The foam breakers draw approximately 10 BHP each. Including necessary pump capacity, the total power consumption runs about 0.25 BHP/GPM. The air to liquor ratio is 15 - 20 CFM/GPM and a retention of 4 - 6 minutes is required on the perforated plates.

Air Sparger Reactors

The air sparged reacters are of two types--air sparging with agitation and without agitation.

Air Sparger With Agitation. Air sparging with agitation is used for both weak and concentrated liquor. This system requires more electric power, it is more complicated, and the equipment cost is higher than for the non-agitation system. The liquor is pumped into a tank where an air header comes in centrally at the top. The header conveys the air into the sparger located approximately six feet from the bottom of the tank. The sparger has a number of arms extending radially from the header and each arm has a number of branches with aeration nozzles. The sparger is submerged ten to fifteen feet in the liquor depending on the desired retention time. The incoming liquor is distributed above the surface in a system of pipes and nozzles. In addition to being evenly distributed, the liquor helps to beat down the foam floating on the surface.

Air Sparger Without Agitation. Air sparging without agitation is used exclusively for concentrated black liquor oxidation. This system operates at about 10 psig air pressure and draws approximately 1.5 - 2.0 BHP/GPM of liquor. The air to liquor ratio is 20 - 30 CFM/GPM and the retention time 2 - 3 hours. Systems with agitation use more horsepower, but should otherwise be comparable.

Effect of Batch and Continuous Digesters

Mills with continuous digesters usually experience higher sodium sulfide loadings than mills with batch digesters. This is attributed to the fact that batch digester systems expose the liquor to more contact with air (primarily during washing) than continuous digester systems, thus resulting in more oxidation of the liquor. For batch digester systems the sodium sulfide content in the weak black liquor storage tanks may be 50 percent of that in the white liquor storage tanks. This condition must be considered when selecting oxidation systems.

Summary

As stated previously, foaming is a major consideration in the selection of an oxidation system. Foaming depends on the wood species, which will contain varying amounts of resin and fatty acid salts. These compounds will create a foam, that in some cases will preclude the oxidation of weak liquor. The foaming is less pronounced in strong liquor. Especially severe is the foaming of liquors from southern pine. The addition of fuel oil or kerosene to the liquor to reduce the foam helps in some cases. Foaming characteristics of the liquor influences the geographical locations of the various oxidation systems. In general, the air sparger type is located in the South due to the resinous content of the southern liquors. Weak liquor oxidation has found extensive application in western United States. The mid-west and northeastern United States have installed primarily weak liquor oxidation systems; however, (1) only one installation is reportedly operating at a high oxidation efficiency. Currently, the general trend in oxidation systems appears to be directed towards more acceptance of the air sparger type for concentrated liquor oxidation.

5.2.8 ORIFICE SCRUBBER

The orifice scrubber is a collection device consisting of a restricted air passage partially filled with water. The resulting dispersion of the water causes wetting of the particles and their collection. Pressure drop is comparable to cyclonic scrubbers.

5.2.9 MESH PADS

Mesh pads are collection devices composed of material such as knitted wire mesh. Dust and liquid droplets are collected on the pads.

A spray washing system is provided for back washing the mesh pads to remove accumulated solid particulate. In normal operation, a maximum pressure drop of approximately 0.2 inches WG is maintained by periodic operation of the spray system.

5.2.10 STRIPPING CONDENSATES

Many condensate streams, especially from the "foul" streams of the MEE, contain TRS compounds. Countercurrent stripping by either air or steam has successfully removed more than 95 percent of these compounds. Thus, the stripped condensate can be used as process water where its use prior to stripping would have resulted in TRS emissions to the atmosphere. It can be used as scrubber water in the smelt dissolving tank, and lime slaking. The stripped compounds are usually incinerated in the recovery furnace, limekiln, or power boiler.

5.3 POWER AND COMBINATION BOILERS, GENERAL

The emission control equipment used in the steam power plants has been almost exclusively limited to removal of particulate matter. Lately efforts have been made to find ways and means to remove sulfur from the fuels and alternatively sulfur dioxide from the flue gases. As yet no commercially economic and feasible method is in operation, but a number of promising pilot studies have been made. The recognition of nitrogen oxides as undesirable compounds in the flue gases is relatively new and efforts in that direction have only begun.

Power and combination boilers in the pulp and paper industry incorporate a wide variety of firing equipment. Some of these types are:

Oil and Gas Burners

Pulverized Coal

Spreader Stokers with Traveling Grates

Spreader Stokers with Vibrating Grates

Spreader Stokers with Water Cooled Grates

Spreader Stokers with Stationary Grates

Spreader Stokers with Dump Grates

Dutch Ovens

Aside from coal the main fuels are oil, gas, and bark. Today the burning of bark for steam generation is confined to locations where bark is available as a waste or by-product. In producing lumber half of the wood in the log is often discarded as saw-dust, bark, shavings, slabs and ends, all of which can be used as fuel. New methods in barking and pulping, however, are continuously reducing the quantity of waste wood available.

The devices commonly used for removal of particulate matter in flue gases of steam boilers are centrifugal collectors and electrostatic precipitators. The following list indicates the type of dust collectors normally used for various types of fuel.

	Mechanical	Electrostatic Precipitators
Coal (pulverized)	X	X
#6 Oil	X	Has been used but is not common
Gas	-	
Bark	X	
Bark + Coal	X	
Bark + Oil	X	
Bark + Gas	X	

Fly ash may be approximately classified according to type of firing as shown in Table 5-1. Fly ash from pulverized coal fired boilers is generally quite fine--about 70 percent (or more) smaller than 325 mesh. It is usually light gray in color as it contains only a small amount of unburned carbon. The small particles, having a large surface area, will impart a definite color to the stack gases. This may, under certain light conditions, indicate that a sizeable amount of fly ash is being discharged into the atmosphere. Fly ash from stoker fired boilers on the other hand is much coarser and has, since it contains larger quantities of unburnt carbon, a dark gray to black color. This fly ash does not discolor the flue gas in the same manner as described above. A clean appearing stack discharge from a stoker fired boiler does not necessarily indicate that there is no emission problem. The coarse particles will fall out relatively close to the stack and on an equal weight basis will cause a greater local nuisance than fly ash from pulverized coal. Thus fine particles make a small plume appear much denser than coarse particles. It is for this reason that removal of particles larger than 20 microns has little effect on the appearance of the plume.

Electrostatic Precipitators

The performance of an electrostatic precipitator is directly related to the level of power input maintained. The amount of electric charge that the dust particles will acquire depends upon the conductivity or resistivity of the dust. When the resistivity exceeds approximately 2×10^{10} Ohm centimeters excessive sparking is to be expected with subsequent drop in collecting efficiency. Research has shown that the resistivity of the fly ash is closely related to the presence of water, soluble sulfates, and free sulphuric acid formed on the surfaces of the dust particles by absorption of SO_3 from the flue gas. If the sulfur content is greater than 1 percent in the coal there is likely to be sufficient SO_3 in the flue gas to create favorable conditions for an acceptable resistivity. However, SO_3 is formed by oxidation of SO_2 which occurs between 750° and 1500°F. The amount of SO_3 formed will depend on the design of the boiler and the rate of combustion. The lower limit of soluble sulfur compounds in the coal ash, necessary to create an acceptable resistivity has been found to be between 0.5 and 1.0 percent. The resistivity also varies with the flue gas temperature and reaches a peak at approximately 300°F for average fly ash. The peak resistivity of some fly ash is high enough to adversely effect the precipitator performance. Yet 300°F is a favorable temperature level for boiler and evaporator operation. Thus, requirements for the boiler and for the precipitators are contradictory. The amount of magnesium and aluminum in the coal ash is also believed to be a factor contributing to high resistivity. Fly ash from strip mined coal usually has higher resistivity than fly ash from deep mined coal.

Fly ash containing more than 15 percent carbon will effect precipitator performance adversely. The reason for this is that carbon is a relatively

T A B L E 5 - 1

TYPICAL PARTICLE SIZE DISTRIBUTION OF FLY ASH FROM BOILER GASES OF VARIOUS BOILERS

(Percent by Weight)

Particle Size Microns	COAL FIRED BOILER					100 Percent Bark Fired Boiler
	Pulverized Coal	Cyclone Furnace	Spreader Stoker	Traveling Grate	Underfed Stoker	
0-10	25%	72%	11%		7%	12%
10-20	24	15	12		8	10
20-30	16	6	9	11	6	7
30-40	14	2	10		9	6
40-74	13		12	12	8	14
74-149	6	5	17	30	19	16
+149	2		29	47	43	35
TOTAL	100	100	100	100	100	100

Data from Bituminous Coal Research Association, Pittsburgh, Penn. and the Industrial Gas Cleaning Institute, "Criteria for the Application of Dust Collectors to Coal Fired Boilers."

good conductor and will acquire, but also loose, an electrical charge very easily. When a particle with high carbon content precipitates on the collector plate it loses its charge immediately. Owing to a phenomenon referred to as "charge by induction," the particle assumes a weak positive charge. It is repelled from the collector plate and reentrains into a gas stream. This phenomenon is repeated over and over again until the particle is carried out by the gas stream and escapes from the precipitator. In order to overcome this problem, the collector plates are given a special form and the so-called pocket or screen grid collecting electrodes have proven to be very effective. There is also a certain correlation between the carbon content and the coarseness of the fly ash. A coarse fly ash has normally a high carbon content.

Recent improvements in the design of electrostatic precipitators have reduced many of the advantages of combinations of electrostatic precipitators and mechanical collection systems, so common some years ago. The plate electrode precipitators did not have sufficient collecting efficiency on high carbon fly ash with problems of "snow outs" from the stack during soot blowing and collector plate rapping periods. Pocket electrodes and continuous rapping have, to a large extent, circumvented these problems. Another advantage of a combined system installation was that the mechanical collector would still remove a major portion of the fly ash should the precipitator be out of order for some reason. Sectionalized design and more reliable rectifiers have shortened the shut-down time considerably on modern precipitators.

Mechanical Collectors

Bark char is a difficult material to collect. While the particle size is relatively large, the specific gravity is very low and the sliver shape of the particles makes collection difficult. Bark char has a specific gravity in the 0.2 range; pulverized coal ash for example, is 10 - 15 times heavier. In addition to the unique particle shape, the low specific gravity and the very fragile particles, the bark boiler collector must also be able to handle abrasive sand accompanying the bark. There are consequently a number of considerations to make when selecting a collector for a bark boiler.

Electrostatic precipitators are not generally suitable for use on bark boilers due to (1) the poor electrical characteristics of bark char and (2) the possibility of fires.

Some studies report that the bark char disintegrates into fine particles in a multi-tube collector due to the high centrifugal forces imposed. These fine particles coupled with their low specific gravity have a tendency to float through the outlet tube of the collector and out the stack. This phenomenon is also attributed to the short distance from the wall of the collecting tube to the outlet tube. A survey shows that there are more large diameter cyclone installations than multi-tube units operating on bark boilers in the wood pulping industry. It should be noted, however, that both collection devices can give sufficient efficiency providing they are selected properly.

Many bark char collectors in the southern part of the United States are operating with reinjection systems that are not equipped with provisions for separation of sand from the char before reinjection. Sand separation is essential for reducing excessive erosion of the collector and the boiler tubes. It is not unusual for a system operating on bark from southern pine to accumulate a number of truck loads of sand in an operating day. Some mills are now selling the collected bark for manufacturing of charcoal briquettes.

In many multi-tube collectors recovery vanes are installed to reduce pressure drop and collector size. The experience shows that collectors operating on boilers firing oil in combination with bark must be designed without recovery vanes. Some oil fractions having high dew-points combine with the bark char particles and plug the recovery vanes. One single plugged outlet tube can by-pass some 10 times its normal share of flue gas uncleaned into the stack. It is consequently imperative to prevent plugging of the tubes.

Studies show that substantial improvement of the collecting efficiency of bark char collectors can be attained by changing the normally conical bottom outlet of the cyclone (tube). By using straight cylindrical tubes with a peripheral discharge rather than conventional conical discharge, the ash is removed from the tube before the gas reverses into the inner vortex and in sufficient distances from the turning point. This prevents re-entrainment of already collected particles.

The volume handled by a given diameter collector tube depends on the shape of the inlet guide vane. Shallow pitched vanes give more spin and handle less volume. Steep pitched vanes reduce the spin and can handle more volume. The shape of the inlet guide vane can make a difference in volume capacity of the tube at a ratio of 1 to 2. The vanes are of obvious importance for collector size as well as operating efficiency.

Bark char collectors should be easily accessible for inspection, maintenance and repair because of the difficult operating condition under which they work. One always has to bear in mind the abrasiveness of the dust and possibility of clogging. Large diameter cyclone collectors are easily accessible for maintenance. Some modern multi-tube collectors also offer design with accent on maintenance. The place subject to wear in a well designed collector is limited to the collection tube or cyclone cone. Hard cast iron is often used in tubes. Hardness of 420 Brinell has proven to be a maximum, because hard tubes are subject to thermal shock damage. Cyclone cones, as well as the entire cyclone, are sometimes furnished with abrasion resistant linings. This lining is usually installed over a hexagonal steel liner.

Both mechanical collectors and electrostatic precipitators are sensitive to uneven gas and dust distribution. The entrance to the collector is normally provided with devices for correction of uneven gas distribution. The space for proper distribution ahead of the collector is almost always very limited. Sharp bends and short transitions tend to produce uneven distribution across the entrance. Various devices such as spreaders, turning vanes and perforated baskets in the collector entrance are used in efforts to overcome these problems.

Hopper fires occur in bark char collectors. Unlike ash from coal fire boilers, bark char must be continuously and completely removed. A small air leakage is enough for accumulated char to catch fire. Gas tight construction is essential in bark char collectors.

Design must consider the possibility and effect of fires. This removal from the hopper must be accomplished without a back flow of air. This can be done most successfully with rotary steel valves.

Bark boiler dust collectors should be carefully sized for correct pressure drop inlet velocity. While efficiency generally increases with increased pressure drop (and velocity) there are limits beyond which fragile material like bark char will be broken into smaller particles which has a detrimental effect on the collecting efficiency.

The low specific gravity of bark char, when the boiler is operated on 100 percent bark without reinjection, or the finer particle size distribution when the ash is reinjected, create operating conditions which limit the application of large diameter cyclones on these installations.

Only when other conditions are superimposed over these conditions can the large diameter cyclone approach 92 percent efficiency in a single-stage unit. One of the conditions which will increase the efficiency is the amount of sand in the bark char.

When operating on 100 percent bark, the efficiency will vary greatly depending upon the amount of sand imbedded in the bark. Without reinjection, much of the imbedded sand remains in the bark char. This greatly increases the average specific gravity of the bark char, making the centrifugal separation easier with higher efficiencies.

Example: 80% Bark Specific Gravity (as char) 0.3

20% Sand Specific Gravity 2.8

S. G. = (0.8) (0.3) + (0.2) (2.8) = 0.24 + 0.56 = 0.80

For a large diameter cyclone where the specific gravity is assumed at 0.3, the most practical unit would give efficiencies in the 70 to 75 percent range. If, as in the example above, the char contained 20 sand, the efficiency would increase to 85 to 89 percent.

The performance of mechanical collectors, with 40 percent bark and 60 percent oil feed to the boiler, is greatly improved due to the higher specific gravity of the fly ash. The nature of this dust, however, in multi-tube collectors creates a plugging problem. The higher specific gravity and tendency not to plug make the large diameter cyclone practical for combination fired boilers. It is possible to achieve the 92 percent design efficiency in both multi-tube and large diameter cyclones with single-stage units. The 96 percent design efficiency is possible with two-stage large diameter or multi-tube units.

5.4 SULFITE SOURCES

The evaluation of control methods for sulfite sources is limited to those which are distinct from the kraft sources. The reader is referred to the previous discussions of kraft sources for the following sulfite sources: Washer vents, evaporators, power boilers, and combination boilers. It should also be noted that control methods have not been considered for the following sulfite sources: Dump tank vent, Venturi absorbers, absorption towers, and ammonia incineration. These sources are either of minor importance from an emission standpoint, or there are no control methods presently in use.

5.4.1 ACID TOWER

5.4.1.1 Application

The pressure accumulator is vented into the acid storage tank because the two tanks are nearby. The acid storage tank is then vented to the absorption tower. This system effectively prevents emissions from these items of equipment, thereby leaving the acid absorption tower as the only significant source of emission in the acid system.

The construction of most absorption towers incorporates a mesh pad distribution system for absorption liquid. Therefore, additional mesh pads are deemed necessary.

The efficiency of absorption of most sulfiting towers exceeds 90 percent. Some mills have placed a second absorption tower in series with the sulfiting unit for scrubbing exhaust gases. This method has been tried only where an existing second tower was available and could be used economically. An example would be the conversion of calcium base, requiring two towers, to ammonium base which requires one tower.

5.4.2 BLOW PIT

5.4.2.1 Application

Two systems were considered to replace the existing multiple wooden blow stacks and showers with a high efficiency SO_2 recovery system as follows:

1. Condenser with Cyclone and Absorption Tower

2. Packed Tower

Flash steam, sulfur dioxide, and inert gases are released in the blow pit during a digester blow. These gases then exit from the blow pit and after the steam is condensed, the noncondensible gases, mainly sulfur dioxide, are absorbed in a packed tower. The recovered sulfur dioxide is reused in the process and the condensate creates a source of hot water.

5.5 VOSC SOURCES

Evaluations of control methods applied to VOSC sources are not included due to the lack of emission data and application experience. The reader is referred to the previous kraft discussions for the following VOSC sources: washer vents, evaporators, combination boiler, and power boiler.

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17. NAPCA, "Tall Stacks - Various Atmospheric Phenomena and Related Aspects," Publication No. APTD 69-12.

18. Wrist, Peter, Mead Corporation, Personal Communication, Sept. 2, 1969.

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CHAPTER 6

FIELD ENFORCEMENT EQUIPMENT

When the FEO visits a pulp mill in order to perform a routine or special inspection, it is not anticipated that he will perform any substantial amount of source sampling. He should, however, carry certain basic equipment and records pertaining to the facility.

6.1 BASIC EQUIPMENT REQUIRED

Normally the FEO will have an official vehicle equipped with a two-way radio to provide adequate transportation and communications equipment. The car should always contain the basic equipment which will make it possible for the FEO to perform his inspection properly, and comply with all applicable safety rules and regulations. The plant manager is responsible for insuring that the OSHA regulations are complied with by his own employees and visitors. Thus the FEO should be prepared to comply with these regulations also. In certain areas it is required that all personnel wear safety shoes, hard-hats, and safety glasses.

The following list indicates the minimum basic equipment which the FEO should carry with him and use: hard-hat, safety glasses, safety shoes, asbestos gloves, coveralls, Ringlemann chart or opacity guide, polaroid camera, compass, wind speed indicator, flashlight, thermometers covering the range 50-800°F, stop watch, 50-foot tape measure, 6-foot rule, manometer, or pressure/vacuum gauge (0-30 inches Hg and 0-10 H_2O), sample containers, thermocouple with portable millivolt meter.

6.2 RECORDS AND FORMS REQUIRED

Prior to the time of his visit, the FEO should review carefully any previous field inspection forms concerning the installation and the permit application form. He should also carry with him on each inspection a copy of the previous field inspection form, a copy of the air pollution code, and a copy of the emergency episode procedures. He also should carry with him on a clipboard a form for recording his observations as well as data obtained from the mill.

6.3 PROCEDURES AND EQUIPMENT FOR SOURCE SAMPLING

In the event that the results of a mill inspection and survey suggest that source sampling is required to evaluate a particular unit, the FEO may have his own personnel conduct the sampling or may require mill personnel to conduct the sampling with an agency employee observing. Regardless of who does the sampling, it is important for the FEO to assure himself that the equipment to be used has been properly calibrated. Generally the agency will be interested in sampling for particulate matter and gaseous sulfur compounds.

6.3.1 PARTICULATE SAMPLING PROCEDURES (AND EQUIPMENT SPECIFICATIONS)

Particulate sampling procedures and the equipment utilized, should essentially conform to that outlined in the Federal Register (EPA) Vol. 36, No. 274, Part II (Dec. 23, 1971), "Standards of Performance for New Stationary Sources."

6.3.2 GASEOUS (SULFUR) SAMPLING PROCEDURES (AND EQUIPMENT SPECIFICATIONS)

This section will outline procedures and equipment descriptions which have been utilized for sampling the major gaseous constituents emanating from wood pulping processes. Currently two basic methods have been developed, sanctioned by the EPA and various states for sampling gaseous emissions, the Barton Titrator and Gas Liquid Chromatograph (GLC).

6.3.2.1 Gas/Liquid Chromatograph (GLC)

Figure 6-1 illustrates the system which may be employed in conveying the gases from the source to the GLC sensing equipment. The stainless steel probe and Teflon sampling line are maintained at temperatures exceeding the dew point of the source gases. The sampling line consists of an insulated, electrically heated 1/4-inch Teflon tube. The sample gases are transmitted to the heated dilution box where they are split into two separate streams. One stream is conveyed to the vacuum source and wasted to minimize lag time in the sampling line. The remainder of the flow is diluted with nitrogen by an amount sufficient to lower the dew point of the gases below ambient temperature. A portion of this diluted sample is injected into the chromatograph through the Gas/Liquid Chromatograph (GLC) sampling valve. The remainder of the diluted gas is wasted through the vacuum source.

Gaseous sulfur concentrations may be determined with a Gas/Liquid Chromatograph. This unit is equipped with a flame photometric detector which is specific for sulfur compounds. Two analytical columns are utilized in the separation and analysis of the gaseous sulfur compounds. One is a 36-foot by 1/8-inch OD Teflon column packed with polyphenyl ether (liquid phase) on a solid support of granular Teflon. The second column, constructed of identical materials, is 8 feet long. Both columns are operated at 50°C.

The 36-foot column is utilized for analyzing hydrogen sulfide, sulfur dioxide, and methyl mercaptan while the 8-foot column facilitates the analysis of dimethyl sulfide and dimethyl disulfide.

Several sampling loops of different volumes may be employed on the GLC sampling valve to accommodate a wide range of gaseous sulfur concentrations.

The chromatograph is calibrated for hydrogen sulfide, sulfur dioxide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, using the "spinning syringe" technique or permeation tubes.

6.3.2.2 Barton Titrator

Figues 6-2 illustrates the system which is employed in conveying the gases from the source to the Barton Titrator. The stainless steel probe and Teflon sampling line are maintained at temperatures exceeding the dew point of the stack gases. The sampling line is identical to the sampling line used with GLC. The sample gases are transmitted to the Barton Titrator by a vacuum source.

Total reduced sulfur (TRS) concentrations are analyzed using a Barton Titrator, Model 400. Furnace gases are scrubbed through a 3% solution of potassium acid phthalate (KHP) which removes sulfur dioxide and a large fraction of water vapor from the sample gases. The scrubbed gases are then passed through a combustion tube maintained above 1500°F where all the remaining reduced sulfur compounds are oxidized to sulfur dioxide. The sample gas is then introduced to a coulometric titration cell which utilizes hydrobromic acid (HBr) as an electrolyte. The electrolytic cell generates bromine from the HBr electrolyte which reacts with the sulfur compounds entering the titration cell. The quantity of current required to generate the excess bromine, to consume the sulfur compound, is proportional to the gaseous sulfur concentrations introduced. The current required to operate the titration cell is sensed and transmitted to a recorder where a continuous readout is accomplished. The recorded output is converted to TRS concentrations, as SO_2, from calibration data generated with the "spinning syringe" technique.

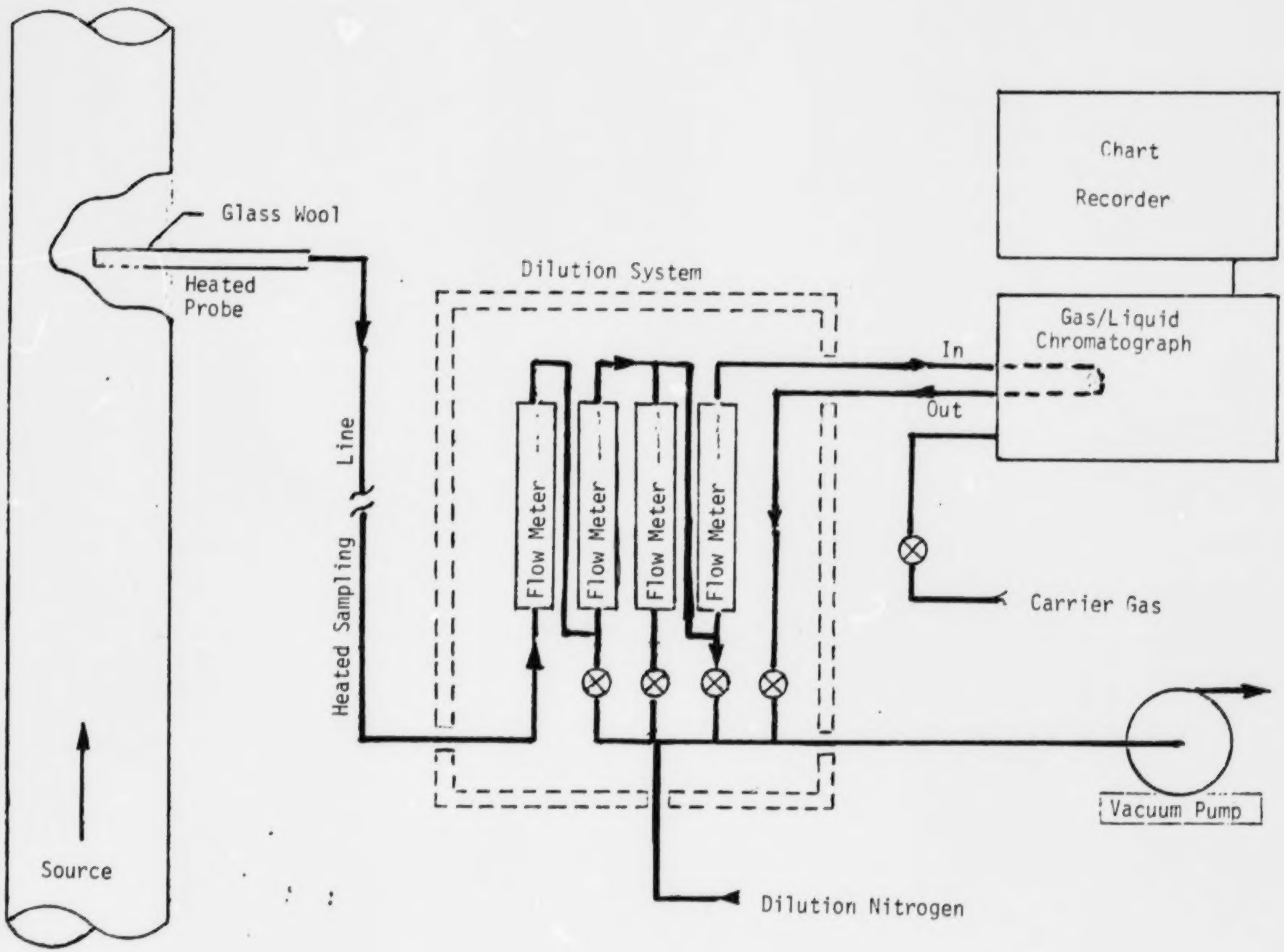
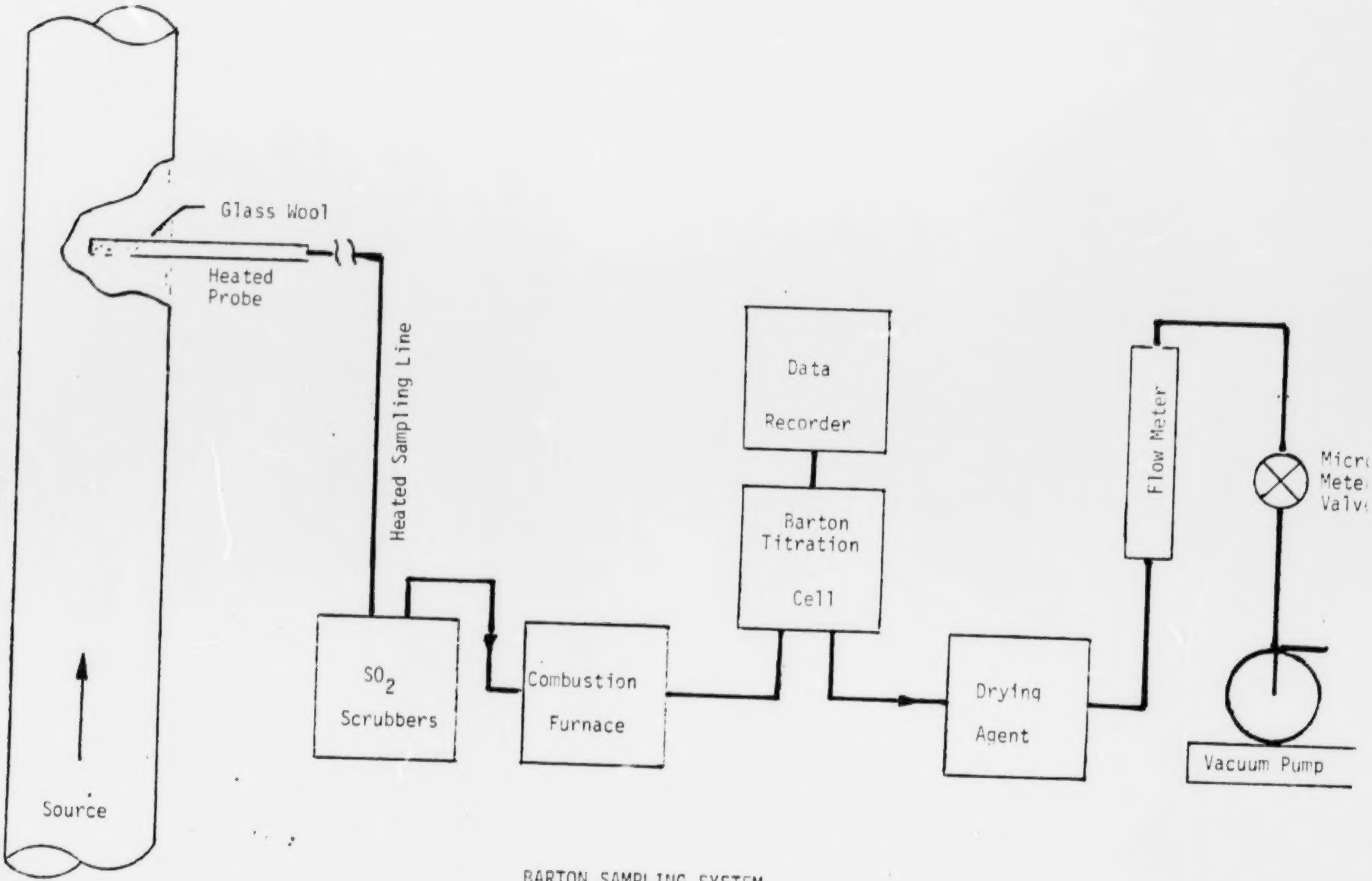


Chart
Recorder
Glass Wool
Heated
Probe
Dilution System
Gas/Liquid
Chromatograph
In
Out
Heated Sampling Line
Flow Meter
Flow Meter
Flow Meter
Flow Meter
Carrier Gas
Vacuum Pump
Source
Dilution Nitrogen

GAS SAMPLING SYSTEM
Figure 6-1


Glass Wool
Heated Probe
Heated Sampling Line
Source
SO_2 Scrubbers
Combustion Furnace
Data Recorder
Barton Titration Cell
Drying Agent
Flow Meter
Micr
Mete
Valv
Vacuum Pump

BARTON SAMPLING SYSTEM

Figure 6-2

CHAPTER 7

UTILIZATION OF FIELD DATA AND RECORDS

7.1 GENERAL INFORMATION

Most states have air implementation plans approved by the Administrator of EPA which contain provisions for a permit system. Normally, a permit is required for both construction and operation of an air pollution source. The plans also require a limitation on emissions of certain compounds to the atmosphere as well as pre-planned strategy for meeting an air pollution emergency.

The application for permit usually requires complete information on the site, a description of the process and process design, and information on the air pollution abatement strategy which is intended to be used. The application states the level of emissions from all parts of the process without any abatement strategy. In an application for a permit to construct, the applicant is required to make an estimate of the level of emission to be expected with the proposed control equipment whereas a permit to operate may not be granted until performance tests are conducted on the source and it can be shown that the source will meet applicable regulations. Usually the regulations require that any modification to the process or any modification to the control devices be reported to the agency. Usually the regulations also require immediate notification of the agency in the case of an upset or emergency condition.

These requirements implicitly call for a continuing program of reports by the holder of the operating permit plus a continuing program of inspection and observation of each source. A visit by the FEO may be triggered by complaints, by reports from the mill, or a routine periodic inspection. Additional information such as complete plans and specifications, operating conditions and similar data may be required by the director of the state agency. All of the information previously cited will form the basis for a file on a specific source.

7.2 FILE OF FIELD DATA

A file on each company (source) should be opened as soon as an inquiry from an official of the company is received at the state agency. The file should contain the completed application for a permit to construct and/or operate with any supporting data submitted by the mill (such as flow diagrams). This file should also contain emissions data collected by the state pollution control staff or the mill staff, copies of permit, copies of complaints, and/or observed violations, and reports on inspections by the FEO. In some instances, the complaint file may be a separate file, depending on the number received, but copies should be placed in the general file for that source.

7.2.1 INDUSTRY DIRECTORIES

Information of a general nature relative to a particular plant may be obtained from one of several pulp and paper industry directories, such as those of Post and Lockwood. An example of pertinent information which may be found in these directories is as follows: (1) Company name and or specific division, location, executive office location, and phone numbers. (2) Production capacity, types of wood pulping processes and raw material consumption. (3) Management personnel and their area of responsibility. (4) Summary of process equipment such as the number of individual units, capacities, manufacturer, and miscellaneous information.

A review of information contained in these sources should be invaluable in assessing the extent and type of survey which should be performed as well as an indication of the technical review required prior to outlining the site inspection.

7.3 ADDITIONAL SOURCES OF INFORMATION

In building up the technical information file on a specific company, and in preparation for an on-site inspection, the following additional sources of information are suggested. A suggested procedure for the on-site inspection is described in the next chapter.

Most pulp mills maintain excellent operating records. The daily operating statistical report and the operating log sheets from the major process areas are somewhat similar from mill to mill. These reports can be utilized to provide the FEO with a profile of operating levels for various mills.

Many pulp mills routinely conduct source sampling tests to determine the performance level of air control equipment. This test may be conducted periodically or continously as indicated in previous chapters. The reports are usually kept on file in the technical department. In some states the results of emission monitoring are required to be submitted to the state agency on a periodic basis.

7.3.1 PROCESS EQUIPMENT SPECIFICATIONS

Quite often, pulp mill equipment capacities are specified by the number of pulp production "tons" which they will support, and this does not relate to the true engineering design criteria. For instance, identical capacity equipment will support a variable pulp production rate, depending on the pulp yield range which is being attained.

Almost all pulp mill production equipment is specified and designed based on pounds of dry solids per unit time processed. These design capacities may be expressed as lbs/hr, tons/day, etc., with further qualifications regarding operating temperatures, inlet and outlet concentrations, etc. With proper conversion factors and pertinent knowledge, it is possible to express specified design capacities in more convenient units for comparisons or other reasons. The Appendix of this report contains information which will assist in converting process material units.

Pulp mill technical personnel may quote "nominal" equipment capacities and specifications when questioned in this regard, which may or may not reflect design and/or actual operating rates. Therefore, the only sure way to determine the actual design specifications is to request a review of the quoted equipment specifications contained in the engineering file, as well as any designed modifications which may have altered the original.

Examples of the type information which may be outlined and summarized in engineering design specifications is illustrated in Tables 7-1 and 7-2, and Figures 7-1 and 7-2 for an evaporator set and recovery boiler.

7.3.2 EMISSION CONTROL EQUIPMENT SPECIFICATIONS

For the major pulping processes, emission control equipment specifications will be tied closely to the process equipment specifications, particularly where the control equipment is an integral part of a "system." In a recently constructed mill, these specifications would be included in a file with the major process equipment. In the case of an older mill, in all probability the control equipment has been updated by modification or replacement, and engineering data and specifications would be contained in a separate file. Control equipment on the miscellaneous sources, because of the various available alternative methods, are usually specified separately as additions to the process. An exception to this may be the case with mills which were built very recently. (See Table 7-3 and Figures 7-3 and 7-4.)

Control equipment design specifications normally stipulate a performance guarantee based on inlet gas volume, grain loading, moisture content, and temperatures. In the case of sub-micron particulate "fume" and gaseous constituents, further stipulation may include quantitative limits on components contained in the process input feed or streams. Design criteria also state static pressure and pressure drop relationships as well as liquid rates and pH in the case of scrubber applications.

Tables 7-4, 7-5, 7-6, and 7-7, contain results of performance tests on several different types of control devices. The data and nomenclature contained in these tables is similar to that which would be itemized in design specifications for similar control devices. More recently the trend has been to specify control systems as a "system" as opposed to individual components. Where a system has been engineered as individual components, it is often difficult to determine the precise performance guarantee point, and where the responsibility and liability lies.

7.4 AGENCY RECORD KEEPING REQUIREMENTS

The FEO must be cognizant of agency record keeping requirements and/or plans. The next chapter of this manual will contain recommended data format sheets, sequential inspection outline, and other pertinent information. The final reporting of data for files, however, may require some individual judgement.

If the agencies involved have not provided specific guidelines in these regards, the inspector may want to make recommendations or suggestions to make files more functional for future reference and site inspection comparisons. These factors will become much more obvious after several pulp mill inspections have been performed. Inasmuch as agency requirements are constantly changing, it would not be appropriate to make concrete recommendations relative to these in this manual.

Table 7-1. Operating Conditions in a Sextuple-Effect Evaporator

Conditions	Flash Tank	IA	IB	II	III	IV	V	VI
Steam pressure								
psi		31.5	31.5	9.4	1.2			
vacuum, in. Hg						8.3	16.2	22.0
Steam temperature, °F		276	276	238	216	196	175	152
Working Temp. drop, °F		24	26	13	13	15	17	24
Liquor Temp., °F	232	252	250	225	203	181	158	128
Boiling pt. rise, °F	14	13	11	7	5	4	3	3
Saturated vapor temp., °F	218	239	239	218	198	177	155	125
Vapor pressure								
psi		9.8	9.8	1.8				
Vacuum, in. Hg					7.4	15.6	21.4	26.0
Latent heat of vapor, Btu/lb		953	953	967	979	992	1005	1023
Pressure drop								
psi		0.4	0.4	0.6				
vacuum, in. Hg					0.9	0.6	0.6	
Vapor pressure								
Next effect, psi		9.4	9.4	1.2				
Vacuum, in. Hg					8.3	16.2	22.0	
Feed, lb/hr	90,605	109,775	135,825	178,815	219,585	251,995	166,520	166,520
Discharge, lb/hr	89,200	90,605	109,755	135,825	178,875	219,585	130,475	121,520
Solids in, %	51.1	42.2	34.2	26.0	21.2	18.4	13.9	13.9
Solids out, %	52.0	51.1	42.2	34.6	26.0	21.2	17.8	19.1
Heating surface, ft^2		4,400	4,400	8,800	8,800	8,800	8,800	8,800
Heating transfer coefficient, Btu/(hr)/(ft)^2/(°F)		174	242	392	386	316	240	190

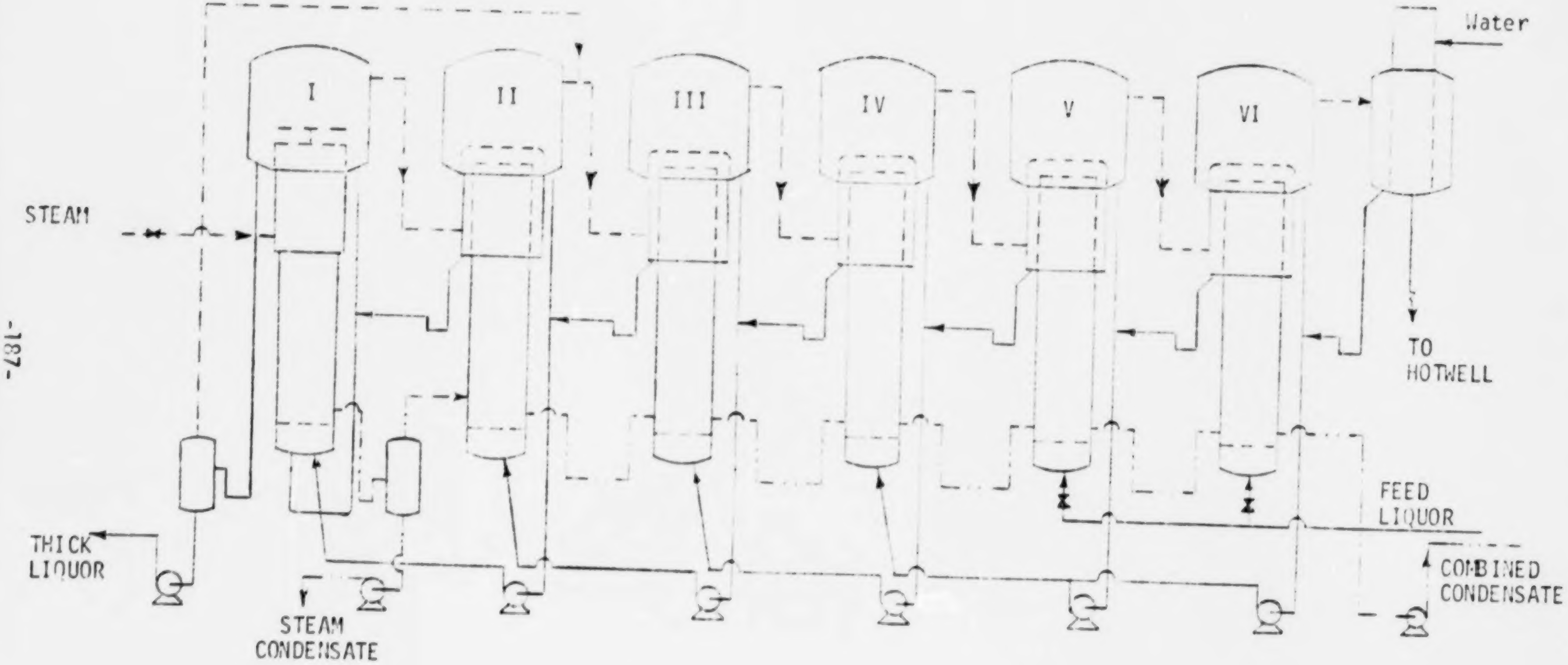

I
II
III
IV
V
VI
Water
STEAM
TO HOTWELL
FEED LIQUOR
COMBINED CONDENSATE
THICK LIQUOR
STEAM CONDENSATE

Figure 7-1. A sextuple-effect evaporator.

TABLE 7-2

COMBUSTION OF BLACK LIQUOR

Typical Operating Performance

Capacity* black liquor at 50% solids	lb/24hr	3,000,000
Black liquor solids	lb/24hr	1,500,000
Steam temperature	°F	825
Steam pressure S.H. outlet	psig	850
Feedwater temperature	°F	275
Air temperature at F.D. fan	°F	80
Air temperature to furnace	°F	280
Gas temperature from evaporator	°F	325
Black liquor temperature to evaporator	°F	200
Salt cake makeup	lb/24hr	62,500

Elemental Fuel Analysis

	Dry solids	Black liquor
Total carbon, %	39.40	19.70
Total oxygen, %	31.40	60.14
Total sodium, %	21.20	10.60
Total hydrogen, %	3.60	7.36
Total sulfur, %	3.40	1.70
Total inerts, %	1.00	0.50
Higher heating value, Btu/lb	6600	3300
Solids content, %		50

Heat Balance

Based on 1lb of black liquor solids (salt cake free)

Datum 80°F

Excess air 15%

Solids 50%

Heat Input	Btu	%
Heat in dry solids	6600.0	93.23
Heat in preheated air from air heater	247.4	3.49
Sensible heat in liquor	180.0	2.55
Heat in moist air	0.0	0.00
Heat in steam to liquor heater	51.4	.73
Total input	7078.8	100.00

TABLE 7-2 (cont.)

Distribution		
Water vapor loss all sources	1593.2	22.51
Dry gas loss	319.6	4.52
Heat of reaction correction	392.8	5.55
Reduction of salt cake	119.8	1.69
Heat of fusion and sensible heat in smelt	233.7	3.30
Radiation	29.7	0.42
Unaccounted for	273.6	3.86
Total unavailable	2962.4	41.85
Heat available for steam	4116.4	58.15
Total distribution	7078.8	100.0
Enthalpy in steam, Btu/lb		1410
Enthalpy in feedwater, Btu/lb		244
Steam, lb/hr		220,600
Quantity		
Steam to liquor heaters, lb/hr		2,790
Flue gas leaving evaporator, lb/hr		429,400
Air to air heater, lb/hr		318,400
Temperature		
Flue gas leaving economizer, °F		648
Smelt temperature, °F		1530
Liquor to furnace, °F		240
Liquor solids		
To evaporator, %		50
From evaporator, %		68
Reduction, %		95
Sulfidity, %		25

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* Before the addition of raw and precipitated salt cake.

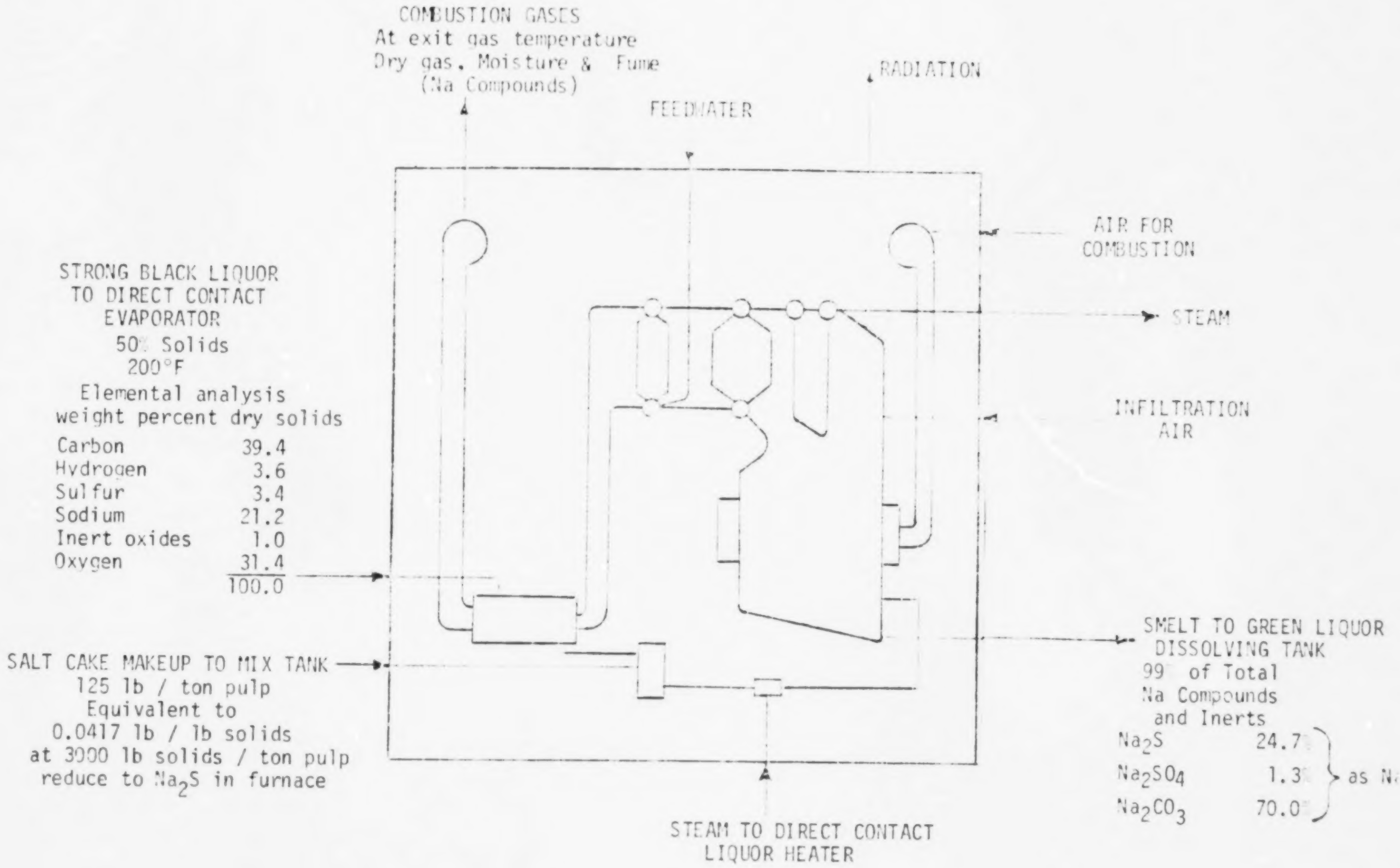

COMBUSTION GASES
At exit gas temperature
Dry gas, Moisture & Fume
(Na Compounds)
FEEDWATER
RADIATION
STRONG BLACK LIQUOR
TO DIRECT CONTACT
EVAPORATOR
50% Solids
200°F
Elemental analysis
weight percent dry solids
Carbon 39.4
Hydrogen 3.6
Sulfur 3.4
Sodium 21.2
Inert oxides 1.0
Oxygen 31.4
100.0
AIR FOR
COMBUSTION
STEAM
INFILTRATION
AIR
SALT CAKE MAKEUP TO MIX TANK
125 lb / ton pulp
Equivalent to
0.0417 lb / lb solids
at 3000 lb solids / ton pulp
reduce to Na2S in furnace
SMELT TO GREEN LIQUOR
DISSOLVING TANK
99% of Total
Na Compounds
and Inerts
Na2S 24.7%
Na2SO4 1.3%
Na2CO3 70.0%
as N
STEAM TO DIRECT CONTACT
LIQUOR HEATER

Figure 7-2. Typical conditions for recovery unit material and heat balance.

TABLE 7-3

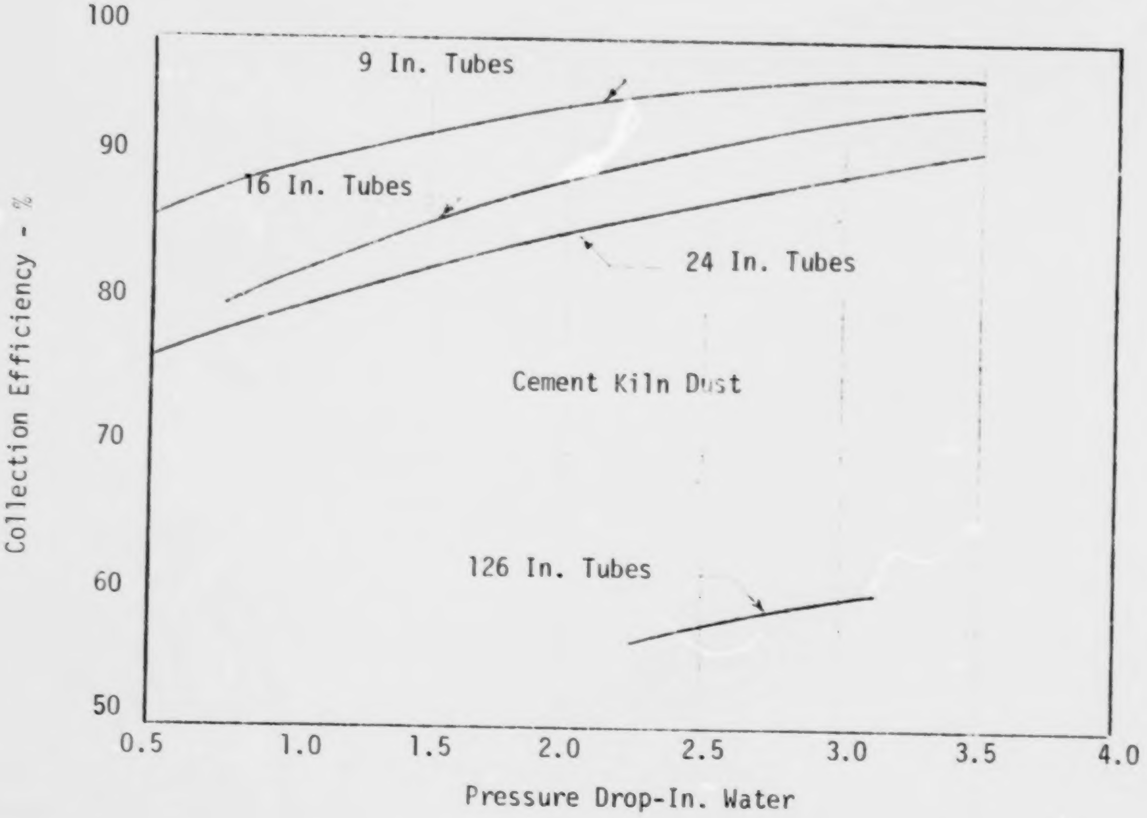
BARK BOILER

DUST COLLECTOR EFFICIENCY TEST

Date of Test:

	BOILER OUTLET	PRIMARY COLL. OUTLET	SECONDARY COLL. OUTLET
Draft Loss		2.0"	2.0"
Gas Temperature (Dry Bulb) °F	640	640	470
Gas Temperature (Wet Bulb) °F	165	170	175
Static Pressure Inches H_2O	-2.5	-4.5	+0.1
Density @ Conditions #/Cu. Ft.	0.0326	0.0315	0.0363
Density @ 70° F. #/Cu. Ft.	0.0681	0.0662	0.0637
Gas Velocity in Duct Ft./Min.	1609	1714	4233
Gas Flow in Duct @ Conditions CFM	279,000	245,960	211,650
Gas Flow in Duct @ 70°F. SCFM	133,613	117,200	120,619
Volume Gas Sampled Cu. Ft.	260.19	213.81	270.48
Sampling Time Min.	35	27	30
Dust Sample Taken Grams	22.7924	1.5658	1.0956
Grain Loading @ Conditions Grains/Cu. Ft.	1.3517	0.1130	0.0625
Grain Loading @ 70° F. Grains/Cu. Ft.	2.8055	0.2345	0.1097
Collector Efficiency %	------	91.64	53.22
Total System Efficiency %	------	------	96.09
Stack Dust Emission #/Min.	------	------	1.89
Total Stack Emission per 24 Hrs. #/Day	------	------	2722

Figure 7-3.



Cyclone Efficiency Vs. Tube Size

Collection Tubes

To capably evaluate dust collectors, the engineer must be aware that there are a wide range of collecting tube designs available, affecting volume of gas handled, draft loss, efficiency, operation, and price. The tube itself is usually of cast iron in a size range between 6 and 24 inches in diameter, nominally 9 inches in diameter for bark boiler service. The smaller 6-inch diameter tube is more efficient, but this is offset by the higher tendency to plug and the higher wear rate of smaller tubes.

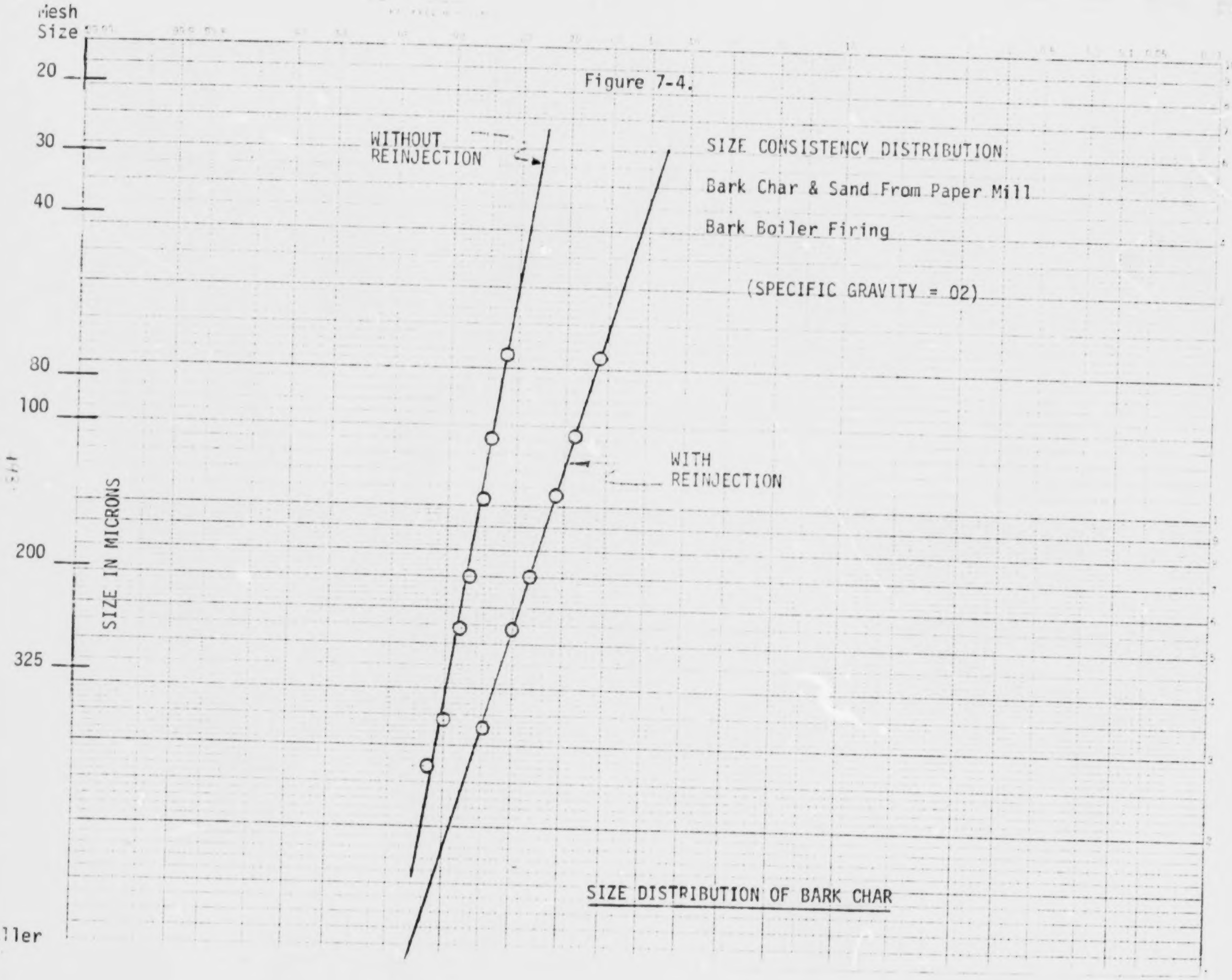


Figure 7-4.

SIZE DISTRIBUTION OF BARK CHAR

TABLE 7-4

Power Boiler Emission Data

FUEL: NO. 6 OIL (NO ADDITIVES)

LBS. STEAM: 100,000 #/HR.

	INLET	OUTLET
Gas Temperature (Wet) (F°)	125	125
Gas Temperature (Dry) (F°)	330	325
Gas Volume @ Standard Conditions (S.C.F.M.)	29,509	30,492
Gas Density @ Standard Conditions (Lbs/Cu. Ft.)	0.0722	0.0732
Grain Loading @ Standard Conditions (Grains/S.C.F.)	0.111	0.0137
Gas Volume @ Conditions (A.C.F.M.)	43,695	45,429
Gas Density @ Conditions (lbs./Cu.Ft.)	0.0494	0.0491
Grain Loading @ Conditions (Grains/A.C.F.)	0.07502	0.0092
Gas Volume Sampled (Cu. Ft.)	10,508	10,855
Gas Velocity (Ft./Min.)	2819	2912
Time Sampled (Minutes)	840	840
Dust Loading (Lbs./1000 Lbs. Gas)	0.2167	0.0268
Dust Emission (Lbs./Min.)	0.4683	0.06
Dust Emission (Lbs./Hr.)	28	3.6

Collector Efficiency: 87%

O = 3%
CO = 13.8%
15.4% Excess Air

TABLE 7-4A

Power Boiler Emission Data

PARTICLE SIZE ANALYSIS

(INLET SAMPLE TO COLLECTOR)

The equivalent micron size is determined from the Bahco analyzer having been standardized with a dust of 2.7 specific gravity but corrected to the actual specific gravity of 1.22.

MICRON SIZE	% BY WEIGHT
1.64 and Below	.66%
1.65 - 2.53	1.79%
2.54 - 5.50	8.78%
5.51 - 10.41	7.80%
10.42 - 15.62	11.26%
15.63 - 24.54	10.94%
24.55 - 31.24	2.16%
31.25 - 35.70	.72%
35.71 - 44.00	.53%
45.00 - 74.00	28.56%
75.00 -105.00	13.34%
106.00 -250.00	11.36%
251.00 -420.00	1.82%
421 and Above	.28%
	100.00%

TABLE 7-5

SUMMARY OF TESTS ON BARK BOILER COLLECTORS

Type Collector - Mechanical, Multiple Tube						
Number Tubes	204	285	384	384	344	340
Type Vane	NR/A	NR/A	NR/A	NR/A	NR/XD	NR/A
Design CFM	152,530	215,000	230,000	230,000	293,000	297,542
Design Temperature	500	725	450	450	679	725
Design Draft Loss	2.73	2.5	2.5	2.5	3.0	3.0
Type Fuel	bark & gas	bark,gas,oil	bark & oil	bark & oil	bark & oil	bark & gas
Rated Steam Load	150,000	300,000	300,000	300,000	300,000	300,000
Bark	150,000	340,000				
Bark & Aux. Fuel	165,000					
Aux. Fuel	200,000					
Steam Load, #/Hr.	150,000	270,000	300,000	268,000	300,000	300,000
Actual Oper. Temp.	460	738	420	410	455-425	640
Actual Oper. D. L.			3.0	2.5	3.5	2.0
MM BTU/Hr. Fired	228	408	457	407	457	457
Max. Rated #/Hr. of Bark	54,700	60,000				
Volume:						
ACFM, inlet	150,190	267,181	222,713	188,510	241,618	279,000
SCFM, inlet	85,323	119,911	134,000	114,800	139,500	133,613
Dust Loading:						
Inlet, #/Day	60,120	93,432	13,940	20,799	47,902	77,592
Outlet, #/Day	4,096	7,464	1,056	1,455	3,509	5,718
Inlet, #/M # Gas	6.797	7.566	1.029	1,804	3.376	5.92
Outlet, #/M # Gas	.497	0.606	.0707	.1052	.2658	0.513
Inlet, #/MM BTU's	10.98	9.54	1.29	2.13	4.36	7.07
Outlet #/MM BTU's	0.75	.76	.0965	.149	.317	0.52
Grain Loading, gr/SCF:						
Inlet	3.426	3.788	.5056	.8805	1.6688	2.8055
Outlet	0.242	0.3027	.0343	.05286	.13018	0.2345
Efficiency of Collection	93.19	92.12	93.36	94.12	92.25	91.64
Allowable Emissions, #MM BTU:						
Georgia and NYC Code	.35	.45	.44	.45	.44	.44
Screen Mesh Size	24	30	14	14	--	20
Notes:			35% bark hardwood 65% oil	79% bark pine 21% oil		

TABLE 7-6

SPECIFICATIONS
Venturi Scrubber

DESIGN INLET CONDITIONS

Volume ____________ CFM
Temperature ____________ °F
Humidity ____________ #W.V./#D.G.
Dust Loading ____________ Grs/SCFD
Density ____________ #/Ft.^{3}

DESIGN EXIT CONDITIONS

Volume ____________ CFM
Temperature ____________ °F
Humidity ____________ #W.V./#D.G.
Dust Loading ____________ Grs/SCFD
Density ____________ #/Ft.^{3}

PRESSURE DROP ALLOWANCES

Waste Heat Evaporator ____________ " W.G.
Kiln ____________ " W.G.
Duct Work ____________ " W.G.
Venturi Throat ____________ " W.G.
Separator ____________ " W.G.
TOTAL ____________ " W.G.

WATER REQUIREMENTS

Scrubbing Water ____________ GPM
Water Evaporated ____________ GPM
Bleed-Off at ________ % Solids ____________ GPM
Make-Up Water ____________ GPM
Water Recirculation ____________ GPM

MATERIALS OF CONSTRUCTION

Venturi Throat ________________________
Flooded Elbow ________________________
Separator ________________________
Duct Work ________________________
Stack ________________________

TABLE 7-6A

Venturi Scrubber Efficiency Test

	Inlet	Outlet
Draft Loss (inches H_2O)	---	22.6
Gas Temperature (Dry Bulb) °F	400	152
Gas Temperature (Wet Bulb) °F	152	152
Static Pressure (inches H_2O)	23	.275
Density @ Conditions (#/cu.ft.)	.0454	.0583
Density @ Standard Conditions (70°F.) 3/cu.ft.	.0695	.0673
Gas Velocity in Duct (ft/min.)	2011	1528
Gas Flow in Duct @ Conditions A.C.F.M.	23207	19208
Gas Flow in Duct @ Standard Conditions (70°F.) S.C.F.M.	15159	16640
Volume Gas Sampled Cu. Ft.	102.72	195
Sampling Time Minutes	24	60
Dust Sample Taken Grams	28.4204	0.3633
Grain Loading @ Conditions (grains/A.C.F.)	4.2692	0.0287
Grain Loading @ Standard Conditions (70°F.) grains/S.C.F.	6.5319	0.0331
Collector Efficiency %	---	99.49
Stack Emission (#/min.)	14.1524	0.0788
Stack Emission (#/hr.)	849.144	4.728
Stack Emission (#/day)	20379	114
Dust Loading (#/1000 # Gas)	13.4146	0.0704
Georgia Code in #/hr. emissions based on process input 6000 #/hr.		8.56

Figure 5-[illegible]

Information Required for Complete Precipitator Survey

COMPANY ______

MILL ______

ADDRESS ______

PERSON TO CONTACT FOR ANY CLARIFICATION ______

PHONE NUMBER ______

Please fill-in or check appropriate blanks.

A. Recovery Information

1. Boiler Manufacturer ______
2. Is this a conventional unit with a direct contact evaporator? Yes ___ No ___

B. Precipitator Design Data

1. Manufacturer ______
2. Gas volume, actual wet cubic feet per min. (ACFM) ______
3. Gas temperature, °F ______
4. Inlet loading to precipitator, grains/SCF ______
5. Outlet loading from precipitator, grains/SCF ______
6. Guaranteed efficiency, % ______
7. Gas velocity in precipitator, feet per second ______

C. Precipitator Construction

1. Number of chambers ______
2. Number of fields ______
3. Dry bottom or wet bottom: wet ___ dry ___
4. If dry bottom, is it a hopper bottom or drag conveyor? Hopper ___ drag ___
5. Does precipitator have a weatherproof [illegible] for the transformer rectifiers? Yes ___ No ___
6. Is the precipitator a steel or tile shell? Steel ___ Tile ___
7. If steel shell, do you have a shell heating system? Yes ___ No ___
8. [illegible] precipitator [illegible] ___ [illegible] ___

D. Collection System

1. Total collecting surface area, square feet ______
2. Height of collecting plates, feet ______
3. Number of collecting rappers ______

E. High Voltage or Charge System

1. Number of transformer rectifiers ______
2. Total output capacity of all transformer rectifiers, [illegible] ______
3. Number of discharge [illegible] ______

F. Rappers

1. Manufacturer ______
2. Type: Electric ___ Pneumatic ___ Weight of [illegible] ______

G. [illegible]

1. [illegible]
2. [illegible]
3. [illegible]

H. [illegible]

1. [illegible]
2. [illegible]

I. [illegible]

1. [illegible]
2. [illegible]
3. [illegible]

Table [illegible]
(cont.)

5. Performance approximately three (3) years after start-up
   Efficiency ______
   Gas Flow ______ ACFM
   Inlet Grain Loading ______ grains/ACFM
   Outlet Grain Loading ______ grains/ACFM
   Gas Temperature ______ °F
6. Performance approximately four (4) years after start-up
   Efficiency ______
   Gas Flow ______ ACFM
   Inlet Grain Loading ______ grains/ACFM
   Outlet Grain Loading ______ grains/ACFM
   Gas Temperature ______ °F

Precipitator Testing

1. Were guaranteed performance tests run on the unit? Yes ___
   No ___
2. What type of particulate test do you use? [illegible]
   (check one): Wet impinger ______
   Dry thimble ______
   Dry thimble & glass filter ______
   Other ______
3. Do you routinely test the precipitator? Yes ___ No ___
   If yes, is this weekly, monthly, yearly, or what? ______
4. What type of particulate test do you perform for routine precipitator testing, if any? (check one)
   Wet impinger ______
   Dry thimble ______
   Dry thimble & glass filter ______
   Other ______

C. Precipitator Operation. (Please give your opinion)

1. Do you have internal corrosion in your precipitator?
   Yes ___ No ___
   [illegible] experienced any corrosion or deterioration of your shell [illegible] you consider serious? Yes ___ No ___ If yes, please explain. ______
3. If a dry bottom unit, do you have any plugging problems in conveying salt cake to salt cake mix tank? Yes ___ No ___
4. Do you consider any of the following to be problem areas (yes or no): Wire breakage ______
   Collecting plate & discharge electrode alignment ______
   Salt cake buildup ______
   If yes, explain where buildup occurs ______
   Wet bottom agitators ______
   Dry bottom hopper ______
   Rapper controls ______
   Transformer-rectifiers ______
   Transformer-rectifier controls ______
   Shut-off gates ______
   Rappers ______

7. Please describe any other problem areas. ______

[illegible] precipitation [illegible] a problem on your unit? Yes ___
No ___
Was your precipitator adequately sized for your requirements? Yes ___ No ___ If no, is this because [illegible] operated above rated capacity? Yes ___ No ___

[illegible]

1. [illegible] Yes ___
   No ___
2. [illegible] Yes ___ No ___ [illegible]
3. [illegible] Yes ___
   No ___
4. Approximately how many [illegible]
5. [illegible] what have you found [illegible] for precipitator maintenance ______
6. Precipitator supplier [illegible]
7. Approximate [illegible] cost ______ /year
   Other costs ______ /year

E. Comments

1. What suggestions would you offer to improve precipitator performance and reliability? ______
2. Other Comments: ______

CHAPTER 8

SITE INSPECTION-ENFORCEMENT PROCEDURE

8.1 GENERAL

The data to be collected and the procedures to be followed are determined by the purpose of the inspection and whether this is an initial or a subsequent inspection.

Specific procedures, especially the citation of violations will depend on the control program and policies of the air pollution agency involved. In general, the inspector performs the following functions: (1) Reporting or verifying progress made by the mill in meeting compliance plan schedules. (2) Verifying any changes from the conditions of the permit. (3) Assuring that day-to-day operation and maintenance practices serve to minimize pollution wherever possible. (4) Reporting breakdown, shut down, or bypassing of process equipment and changes in pulp production schedules or cooking and chemical recovery procedures. (5) Citing violations that are clearly flagrant in nature. (6) Correlating public complaints with air quality measurements, emission rates, and control practices. (7) Noting any new sources, new or modified control devices, and changes in pollution control personnel since the last visit. (8) Reviewing the emission data collected by the plant staff and comparing it with reports submitted to the control agency.

In all cases certain general procedures should be followed including: (1) off-site observations, (2) interview with plant personnel, (3) in-plant observations, (4) critique and meeting with plant management, and (5) observing safety precautions.

8.2 OFF-SITE OBSERVATIONS

Before entering the plant, the inspector should observe and note any visible emissions and odors, dustfall in the surrounding area, possible vegetation damage, and/or effects on materials and paint. These findings should be correlated with public reactions in neighboring communities and with specific mill operations wherever possible.

The inspector should note wherever possible wind directions, wind speed, humidity, and atmospheric stability in his observations, and he should develop a systematic procedure for patrolling and noting the location, quality and intensity of the odor. Odors may be noted on an intensity scale or a scentometer may be used. The inspector may organize a community odor panel consisting of carefully selected citizens who may help to establish the significance of day-to-day ground level variations within the normal odor intensity range. An expert odor panel working under controlled, closed room conditions may also help to isolate the effect of possible changes in mill operations (1).

Sulfur compounds (particularly H_2S) can discolor and damage lead based paints and paints containing mercury-based fungicides and may accelerate tarnishing of silver and copper. Discoloration usually takes the form of browning or blackening of materials and is enhanced if the surfaces have been moistened or weathered, depending on the lead content. Fungi will also darken unprotected paints, so the inspector should, in doubtful cases, have the cause of damage verified by experts. Vegetation damage also may result from sulfur dioxide emitted from boiler equipment, as well as from hydrogen sulfide.

Deposits of particulates may result from the fallout of saltcake particles, fly ash, soot, burned particles, and lime, which are usually confined to within 1/4 to 2 miles from the plant. Some of the fallout is of a comparatively caustic nature and can damage vegetation, materials and painted surfaces particularly on vehicles located near the plant. Particles may be sampled and taken to the laboratory for analysis to help identify the process sources responsible. Particles high in calcium are generally emitted from the lime kiln; particles high in sodium may originate from the recovery furnace and smelt tank; charred or insoluble material originates from hog burning equipment. Sodium salts, which tend to be more volatile than other particulates, may be due to floccuiation of particles in the electrostatic precipitator. These consist of fluffy aggregates up to 1 millimeter in diameter (5). The larger aggregates are largely responsible for damage to paint and vegetation.

All observations should be carefully documented including the date and time, and weather conditions (especially wind speed and direction). In reading visible emissions, the recommended procedures regarding location of observer in relation to plume and sun must be followed.

Points of emissions in a pulp mill include stacks and vents at roof level, the recesses between plant structures, inside the structures, and ground level. The obvious emissions are the steam plumes and mists, particularly from the recovery furnace. These can be voluminous and may travel over great distances and altitudes. The steam and vapor emissions make it difficult to isolate and read the dry portions of the plumes. Long plumes, however, are always suspect in view of the relatively rapid dissipation of steam. Reading visible emissions, while taking into account the dry and liquid contaminants is tenable, but the practice will depend on the policy of the air pollution control agency involved.

The inspector should become familiar with the quality and intensities of odors and the visual character of mill emissions as they vary through the day and with weather conditions. Where abnormal conditions occur, source testing should be requested. Where a large number of public complaints are reported, the possibility of odors being released with intermittent emissions from starting up and shutting down of equipment, opening of digesters, condenser or heat recovery system failure, and overloading of recovery furnace, should be investigated. Vents on bleaching and other mill operations, also, should not be ignored, as chlorine gas can be accidentally released.

8.3 INTERVIEW WITH PLANT PERSONNEL

Direct discussion with both management and operating personnel will enable the enforcement officer to gain a complete understanding of the plant schedule and operation, and allow plant personnel to understand the officer's purpose for this inspection. If a violation has already occurred, the responsible persons should be notified and the reason for the violation determined.

Establishing a good rapport with the plant staff will be most important in obtaining process operating information, descriptions of start-up conditions, number and extent of upsets, equipment breakdown problems, and related information.

In pulp mills, the interview is usually conducted with staff that has been permanently assigned to the air pollution problems of the plant. The interview should be primarily directed at ascertaining factors which affect process emissions, control progress and changes in operating procedures which cannot be noted during the physical inspection. Recording charts, logs and charts relating to process performance and emissions can be examined in the office with the air pollution staff of the mill. The inspector should clearly establish normal operating procedures in order to be able to identify abnormal or changing conditions. A procedure should be adopted and practiced by which the mill reports upsets and outages to the enforcement agency. Scheduled maintenance, especially if it involves taking control equipment out of operation, should be announced in advance.

The exact nature of an interview will vary with the purpose of the visit. For an initial visit an extensive review of the process equipment, layout, and operating schedule will be required. Subsequent visits will require less time and consist only of a review to make sure nothing has changed, or if changes have occurred, to check their effect on emissions.

Information obtained by interview should include:

1. Type of Wood Used: resinous content, softwood, hardwood extent of use of saw dust, etc. The methyl group contained in certain sulfur based emissions derive from the methoxyl content of woods. Hardwoods contain more methoxyls than softwoods, and have greater process odor potential (7).

2. Cooking Variables. Malodorous emissions can be increased when cooks are shortened and pressure and temperatures are increased.

3. Pulping Capacity of the mill should be determined in terms of tons of unbleached air dried pulp. The inspector should become familiar with variations in pulping capacity. Substantial increases in pulping output may cause the capacities of existing process equipment to be exceeded, including overloading of the recovery furnace, and excessive emissions from power plant and other supporting equipment.

4. Plant program for monitoring emissions. The inspector should be familiar with the mill schedule for conducting source testing and maintenance of continuous monitors, such as the titrator, discussed later. It is extremely important that the equipment be kept in good working order. The inspector should clearly establish any modifications made by the plant to the instrumentation, and should assure that a formal procedure for maintaining the accuracy of continuous monitors be adopted.

5. Emission inventories, negotiated compliance plans and permits. The inspector should have available with him information concerning the equipment and emission inventories of the plant to determine if significant changes have been made in any of the major sources that will affect emissions and odors. It is desirable to compare operating permit, inventories, process flow diagrams, and plot plans on file with existing conditions. This can be accomplished either before or after the tour through the plant. The liquor flow, the exact points of emission and firing rates to the recovery furnace, the lime kiln and the power boilers and hog burners, in particular, should be noted.

6. Frequency of conditions under which excessive emissions might occur, such as start-up, soot blowing, ash removal, peak loads, etc. should be discussed and noted.

Interviews also present a good opportunity to discuss future plans for changes in the operation such as expansions and/or major modifications. The personnel interview is also an excellent time to review emergency action plans and discuss the feasibility and time schedule required to implement the plan.

8.4 IN-PLANT OBSERVATIONS

The field enforcement officer upon entering the plant property should ask for the plant manager and state his name, affiliation, and purpose. In most cases, his visit will have been prearranged and he will have a firm appointment. However, on occasion, a random visit or a visit based on an off-site observation will be made. During such times, the plant manager may not be available and a lower ranking member of management or technical staff should be requested.

While inside the plant boundary, the inspector should again note the general "housekeeping" practices within the plant; i.e., is the plant equipment well maintained, are the roadways dust covered or littered, is equipment kept clean and painted. These general observations will give the inspector a feel for the care taken in preventing excessive atmospheric emissions.

Additional visible emissions and/or odor observations can be made on-site, especially if vents were not visible from the plant boundary.

8.4.1 EQUIPMENT INSPECTION

The field enforcement officer should visibly inspect the process equipment, any control devices, and all appurtenances. Nameplate data and ratings should be checked and the degree of maintenance and operability of all equipment noted. Operational data such as temperatures, pressure drop, steam rates, auxiliary fuel use, etc. should be noted where available. He should be especially cognizant of unusual operating conditions such as excessively high or low load.

A visual inspection will also indicate the operability and care given to the instruments and control systems used to monitor and operate the process.

8.4.2 DETERMINATION OF OPERATING CONDITIONS

An assessment of the operating conditions, and their related effect on emissions, can be performed in a comprehensive manner provided adequate preliminary evaluations have been performed, i.e., following the pre-survey review of the mill, review of state permit applications, and review of the process and control equipment specifications. If these reviews are performed comprehensively in the proper sequence, it is conceivable that in the case of well maintained mills with good operating records, and with the assistance of proper data, a site evaluation could be performed requiring very little time in the process areas. The source of this information and operating data is the daily operating statistical report and the operating log sheets from the major process areas.

Figures 8-1 through 8-7 contain plots of some of the more pertinent measured variables and their relation to emission levels associated with the kraft recovery furnace operation. Similar relationships for other kraft processes, and other pulping processes, may be found in Chapters 2 and 3, or may be derived from the discussions contained in these same chapters. Tables 8-1 and 8-2 have been prepared to assist field enforcement personnel in conducting their surveillance of operating variables and conditions relating to atmospheric emissions.

8.4.3 ASSESSING CONTROL EQUIPMENT OPERATING CONDITIONS

Pertinent control equipment operating variables are also monitored with in-line instrumentation which are also shown on process flowsheet instrumentation schematics as previously discussed. The important variable values are also recorded on the appropriate process operating log sheets.

The optimum level of these variables, as required to maintain maximum performances, are normally stipulated in the formal design specifications. Principles of operation for all types of control devices have been discussed in Chapter 4 and effects of operating variables have been discussed in Chapters 2 and 3.

8.4.4 ESTIMATING EMISSION RATES

The appendix contains a series of graphs developed by NCASI, which relate atmospheric emissions from various sources in the kraft pulping process, to pulp production rates. The basis used to derive these relationships is clearly stated, and correction factors must be applied to these data if the basic process basis differs appreciably from that stated. This data can be used effectively to determine nominal levels, to compare operating data and estimate emission levels where data is not available.

8.4.5 SOURCE SAMPLING RESULTS CONDUCTED BY MILLS

Many pulp mills routinely conduct source sampling tests periodically to determine the performance level of their control equipment. The results of these tests are usually the subject of an informal report for inter-company use. These reports are kept on file in the technical department and should be available for review by enforcement officials. This is another source of information which may be used to assist enforcement officials in developing their site inspection plan.

8.5 CRITIQUE AND MEETING WITH PLANT MANAGEMENT

An effective air pollution control program cannot be conducted at a pulp mill unless it has the whole-hearted endorsement of management. It is important therefore that the inspector discuss all of his major findings both good and bad with top mill management. At the least, this should include the mill manager and the technical director. Those personnel who accompany this inspector on his inspection should also be present. It is especially important to inform the top management of the mill of any adverse findings as well as the need for new equipment or new programs. It is also important to inform them of especially effective work done by the mill employees.

8.6 SAFETY PRECAUTIONS

The field enforcement officer must obey all safety precautions during his visits, whether or not they are required by the plant. As a rule the enforcement officer should not sign accident waivers when entering a plant. He should, however, have his own personal safety equipment such as a hard hat, eye and ear protection, and safety shoes, etc., as detailed previously. On a first visit to a plant, he should review all safety rules with plant personnel. The inspector should never tour the plant without an escort, nor should he open furnace doors, manipulate valves or controls, or in any way try to change the operating characteristics of the unit. When observing the combustion chamber interior, he should always have the operator open the viewing ports, and always use proper eye and face shields.

Due to a large number of fans, belt and chain drives, electrical motors, etc., the inspector should be especially aware of the hazards associated with this type of equipment.

The inspector should not climb on ladders, scaffolds, etc. unless they meet the appropriate safety standards.

As a general rule, the inspector should not take any action which he feels could in the slighest way cause a safety hazard to himself or other plant personnel.

8.7 SPECIAL PROCEDURES FOR KRAFT MILLS

The physical inspection should be organized around two closed systems: (1) The black liquor system including the digestors, relief valves, accumulators, oxidation towers (if used), multiple effect evaporators, direct contact evaporator, recovery furance, and smelt tank. (2) The lime recycling system including the mud filter, lime kiln, and slaker.

The bleaching plant should also be inspected, particularly the brown stock washer, where water vapor and malodorous compounds may be collected by a hood and discharged to the atmosphere.

The principal odors from a kraft mill are characteristic in terms of their quality and pervasiveness. Tables 8-2 and 8-3 illustrate odor thresholds, and qualities of sulfur compounds (1). Other odors such as terpenes and methanol differ significantly from hydrogen sulfide and mercaptans, and are easily recognized. These have the odor of turpentine or are "medicinal" in character, and tend to be localized around process equipment, particularly stock washers, and oxidation towers. The sulfides and mercaptans, by contrast, can be detected many miles from the plant.

8.7.1 BLACK LIQUOR SYSTEM

Although the recovery furnace is the most significant unit from the viewpoint of the emission of particulate matter and TRS compounds, the inspector should visit all the other units previously described for this system. The inspector should become familiar with the vents, valves and condensers, the type of condensers, and associated odors and emissions. The design, condition, and operation of all other units should be noted as these have a bearing on the release of odors from the furnace. Spills, indications of poor maintenance, and low level odors should be noted at each unit. It is necessary also to determine what treatment is applied to malodorous gas streams.

Not only is the recovery furnace the most important source of emissions in the black liquor system, but the operator of the furnace maintains a daily operating log which contains information from other parts of the system.

The inspector should become familiar with the specific design and operation of the recovery furnace in the plant to which he is assigned. Many factors enter into achieving optimum combustion in the furnace from an air pollution standpoint, including the firing rate, secondary air flow, percent excess oxygen in the flue gas, black liquor spray droplet size, time, and turbulence. In the recovery furnace control room, the following items (usually entered hourly) should be checked on the operators log sheet or by instrument readings: (1) Sulfidity of white liquor (in some mills the sulfidity of the green liquor is measured), (2) percent solids of the black liquor, (3) sodium sulfide content of black liquor in and out of the black liquor oxidation unit (if one is used), (4) excess oxygen in flue gas, (5) rate of excess air and secondary air, (6) black liquor firing rate, (7) combustibles, (8) TRS emissions (Barton), (9) frequency and time of soot blowing, (10) steam production, and (11) voltage and amperage readings of the electrostatic precipitator.

All of the above items should be correlated with recovery furnace emissions, so that overloads can clearly be recognized from the performance data.

It should be noted that increased sulfidity usually results in higher TRS emissions. Also it is important to note the relationship of TRS, combustibles, and excess oxygen. When TRS increases, combustibles also show an increase, but excess oxygen will show a decrease, and vice versa. Excess oxygen readings below about 3% may indicate furnace overloading, and/or may indicate an increase in TRS emissions.

The inspector should check to see whether the air ports in the recovery furnace are regularly rodded to prevent plugging and that excess oxygen and proper operating temperature (usually around 1100°F) are maintained in the upper oxidation zone of the furnace. A decrease in secondary air for any reason can cause an increase in emissions. The inspector should recognize however, that steps may have to be taken on occasion to prevent dangerous situations such as furnace reaction explosion.

8.7.2 LIME RECYCLING SYSTEM

The lime recycling system may be a source of both particulate and odorous emissions. The makeup rate for salt cake (pounds of salt cake added per ton of pulp produced) indicates how much of the sodium and salt cake is being lost to the atmosphere and to wastewater reuse or treatment. A loss of 100 pounds of salt cake per ton of pulp may be reasonable, but the proper figure must be established with each plant. This information generally will be found in the recovery furnace log sheet. Hydrogen sulfide may be emitted from a kiln stack, particularly in long kilns, due to reactions of carbon dioxide with sodium sulfide in the carbonate sludge, and to the introduction of carbonate at the cooler end of the kiln. In some plants non-condensible gases are carried to the lime kiln for incineration.

Operational data for this system usually will be found in the operators log at the lime kiln control room. The following lime kiln operational data should be obtained from the log sheet: (1) sodium and sulfide content of washed cake (usually taken once per day or per shift), (2) scrubber water flow rate and source (usually taken once an hour), (3) scrubber pressure drop by manometer, and (4) TRS emissions (Barton).

It should be noted that large variations occur in emissions from different mills using the same process, making the same products, from the same wood species. Even in the same mill large variations may occur from hour to hour.

8.8 SPECIAL PROCEDURES FOR SULFITE MILLS

The sulfite segment of the pulp industry, unfortunately, cannot be as readily categorized as the kraft segment. There are four chemical bases for cooking liquor, four pH ranges for the liquor, and about twenty schemes for recovery of the cooking liquor. Thus the number of possible combinations far exceeds the 33 sulfite mills reportedly operating in the United States in 1973.

Whillte (12) has published a comprehensive review of sulfite and bisulfite recovery systems. He concluded that the only proven technology for recovery of both base and process sulfur is for magnesium base sulfite liquors.

Generally speaking, the principal emissions are sulfur dioxide and particulate matter and the major source of SO_2 is the blow tank of an uncontrolled mill. In most sulfite mills the SO_2 emissions from the various sources are recirculated several times through the absorbers to boost the sulfite content of the cooking liquor.

For these reasons, an inspection itinerary which would be applicable to even a majority of the mills is virtually impossible. Since there are no more than 9 or 10 sulfite mills in any state, it is recommended that the FEO work closely with the technical staff of each mill to establish an inspection protocol.

8.9 SPECIAL PROCEDURES FOR NSSC MILLS

As in the case of sulfite mills, there is considerable difference among NSSC mills. In fact, many of the existing mills were converted to NSSC from other types of pulping. Thus, categorization of this segment of the chemical pulp industry is virtually impossible.

Emissions to the atmosphere from NSSC pulping depend largely on the method of handling the spent cooking liquor. Nearly half of the NSSC mills is the U. S. sewer the liquor and treat it as a liquid waste. Nearly as many mills attempt recovery of heat and chemicals by introducing the spent liquor into a smelter or recovery furnace (either its own or that of a neighboring kraft mill). Since the spent NSSC liquor has a lower pH than the spent kraft liquor, a mixture of the two results in an increase in emissions of SO_2 and H_2S from the kraft recovery furnace. According to Galeano (13), the principal emissions are particulate matter, SO_2 and H_2S. The major sources appear to be the recovery furnace or smelter, the sulfiting tower, and the blow tank.

Because of the lack of data on emissions from the NSSC process, especially on the variation between mills, an inspection itinerary which would be applicable to even the majority of the U.S. mills is impossible. Since there are no more than 4 mills using the NSSC process in any state (roughly 40 in the U. S. in 1973), it is recommended that the FEO work closely with the technical staff at each mill to establish an inspection protocol.

TABLE 8-1

KRAFT PULP MILL

PERTINENT NOMENCLATURE AND TYPICAL VALUES

Active alkali on ovendry wood, lb/lb	0.167
Active alkali concentration, lb/ft^3	7.0
Effective alkali on ovendry wood, lb/lb	0.14
Normalizing value of effective alkali, lb/lb	0.15
Capacity of digesters (a.d. tons), tons/batch	14.5
Specific heat of wood solids, Btu/(lb)(°F)	0.33
Caustic conversion efficiency, nondimen	0.78
Evaporator steam economy, nondimen	4.66
Solids fraction in liquor to furnace, nondimen	0.545
Solids fraction in liquor to evaporator, nondimen	0.188
Blow flow rate, lb/ton a.d. pulp	1516.
Water in liquor from evaporator, lb/ton a.d. pulp	2519.
Evaporation rate from evaporator, lb/ton a.d. pulp	10,549.
Water in liquor to evaporator, lb/ton a.d. pulp	13,069.
Heat capacity of digester contents, (Btu/°F)/ ton a.d. pulp	11,845
Heat of combustion of lignin, Btu/lb	8100.
Heat of fusion of smelt, Btu/lb	530.
Heat produced in recovery process, Btu/ton a.d. pulp	7.96×10^6
Total sulfur loss fraction, nondimen	0.337
Total sodium loss fraction, nondimen	0.0931
Number of digesters, nondimen	5.
Production rate, tons a.d. pulp/day	500.
Furnace reduction ratio, nondimen	0.976
Liquor-to-wood ratio, lb/lb	2.8
Sulfidity of cooking liquor	0.323
"Effective" sulfide in cooking liquor, lb/lb wood	.0539
Solids in smelt, lb/ton a.d. pulp	1208.
Black liquor solids in liquor to evap., lb/tons a.d. pulp	3018.
Usage of kiln fuel, MBtu/ton NaOH	8.84
Usage of makeup lime, lb/lb NaOH	0.0276
Volume of black liquor to digesters, ft^3/ton a.d. pulp	13.6
Volume of total cooking liquor, ft^3/ton a.d. pulp	104.
Volume of white liquor, ft^3/ton a.d. pulp	90.4
Weight of wood fiber, lb/ton a.d. pulp	1800.
Weight of wood lignin, lb/ton a.d. pulp	1989

KRAFT PULP MILL
(Continued)

Moisture content of wood (fraction), lb/lb	0.52
Weight of wood solids, lb/ton a.d. pulp	3789.
Total weight of wet wood, lb/ton a.d. pulp	7895.
Weight of wood water, lb/ton a.d. pulp	4105.
Weight of caustic (as Na_2O) in cook, liquor lb/ton a.d. pulp	428.4
Weight of sulfide (as Na_2O) in cook liquor, lb/ton a.d. pulp	204.4
Weight of sulfate (as Na_2O) in cook liquor, lb/ton a.d. pulp	5.0
Weight of carbonate (as Na_2O) in cook liquor lb/ton a.d. pulp	120.8
Weight of makeup salt cake (as Na_2O), lb/ton a.d. pulp	70.58
Weight of makeup carbonate (as Na_2O), lb/ton a.d. pulp	0.06
Pulping yield, nondimen	0.475

Table 8-2

Pertinent Operating Parameters Which May Affect Atmospheric Emissions from Kraft Pulping Operation

(To Be Used By FEO In Developing Site Inspection Route And Data Collection Format)

Digester Room Log (Pulp Production)

Chip weight charged, tons
White liquor charged, gallons
Actual cooking time, minutes
Number of cooks blown per 24 hour period,
    Hard Stock
    Soft Stock
White liquor sulfidity,

Recovery Boiler Log

Steam flow, 1000 lbs per hour
Gas temperature boiler outlet, °F
I.D. fan setting
I.D. fan speed
Total air flow, CFM or pounds per hour
Primary air flow, CFM or pounds per hour
Secondary air flow, CFM or pounds per hour
Tertiary air flow, CFM or pounds per hour
I.D. fan inlet draft, inches water gage
Precipitator inlet draft, inches water gage
Dissolver tank vent draft, inches water gage
Demister Pads
Black liquor flow to burners, lbs per hour
Black liquor pressure, lbs per square inch
Black liquor solids, percent
Fuel oil flow, gallons per minute
Saltcake feed, pounds per hour
Combustibles, percent
Excess air, percent

Precipitator Operation

Inlet, volts, amperes, milliamps and spark
Outlet, volts, amperes, milliamps and spark

Table 8-2 (Continued)

Lime Kiln Operating Log
Feed mud solids, percent
Feed flow, GPM
Mass flow, tons per day
Oil pressure, psi
Cold end temperature, °F
Hot end temperature, °F
I.D. fan inlet vacuum, inches water gage
Scrubber inlet pressure, inches water gage
Scrubber outlet pressure, inches water gage
Fresh lime rate, tons per day

Barker Boiler Operation
Steam from oil, lbs per hour
Steam from bark, lbs per hour
Oil flow, gallons per minute
Screw feeder speed, RPM
Bin level, feet
CO_2, percent
Over fire air pressure, inches water gage
I.D. fan draft at inlet, inches water gage
Gas temperature leaving boiler, °F

Power Boiler Operation
Fuel oil supply pressure, psi
Under-grate air flow, ration (or oven-fire)
Oil burner windbox pressure, inches water gage
I.D. fan inlet draft, inches water gage
CO_2, percent
Gas temperature leaving boiler, °F

TABLE 8-3

ODOR THRESHOLDS OF KRAFT MILL GASEOUS SULFUR COMPOUNDS IN AIR

ppm (by volume)

Sulfur Dioxide	1.0-5.0
Hydrogen Sulfide	0.009-0.0085
Methyl Mercaptan	0.0021-0.040
Dimethyl Sulfide	0.0001-0.0036

TABLE 8-4

CHARACTERISTICS OF KRAFT MILL GASEOUS SULFUR COMPOUNDS

Compound	Characteristic Odor	Color	Explosive Limits (air) Lower	Upper
Sulfur Dioxide	strong, suffocating	none	Not explosive	
Hydrogen Sulfide	rotten eggs	none	4.3%	46%
Methyl Mercaptan	rotten cabbage	none	3.9%	22%
Dimethyl Sulfide	vegetable sulfide	none	2.2%	9%

Figure 8-1

EFFECT OF CHLORINE IN BLACK LIQUOR

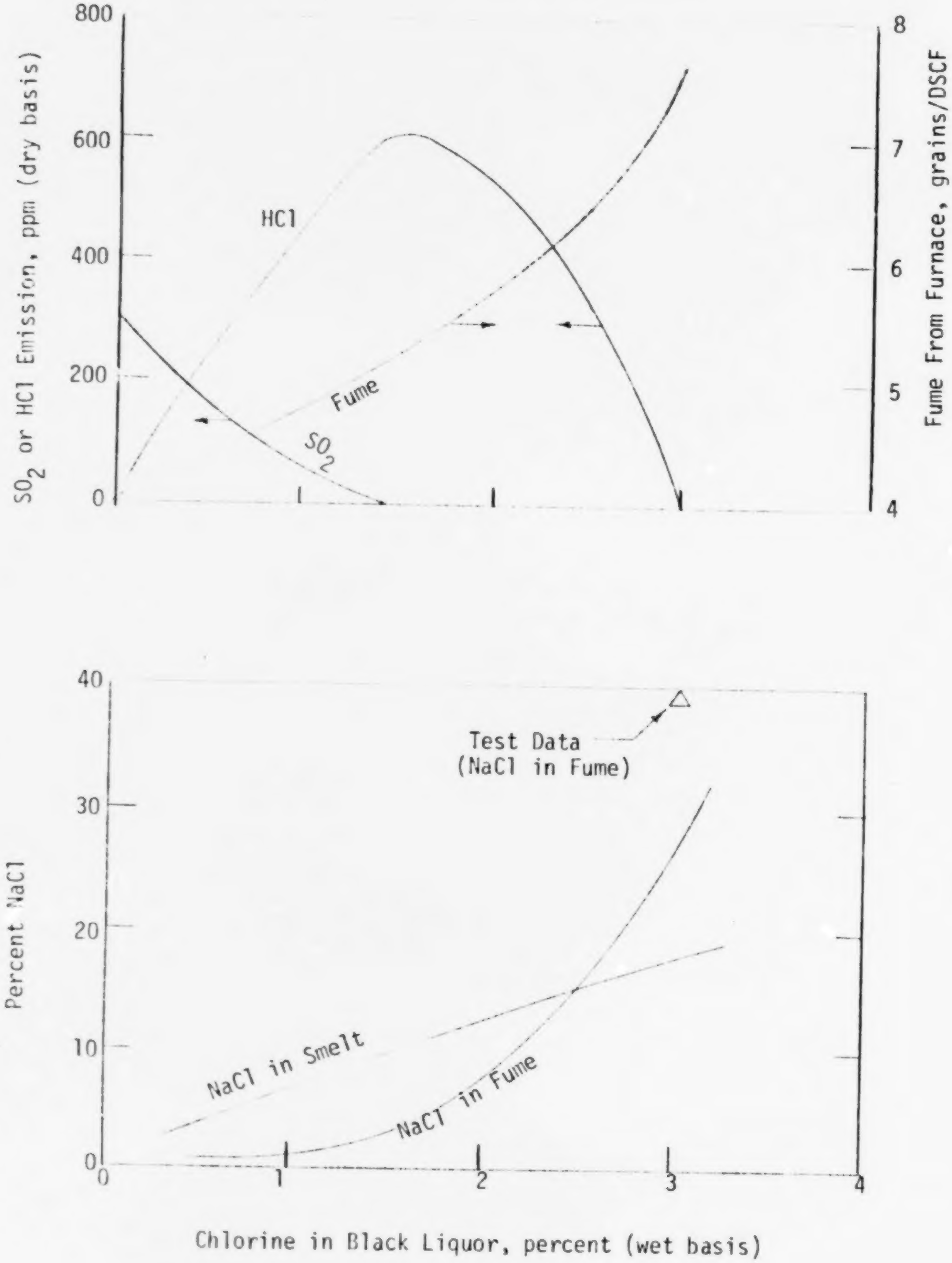


Figure 8-2

EFFECT OF BLACK LIQUOR HEATING VALUE

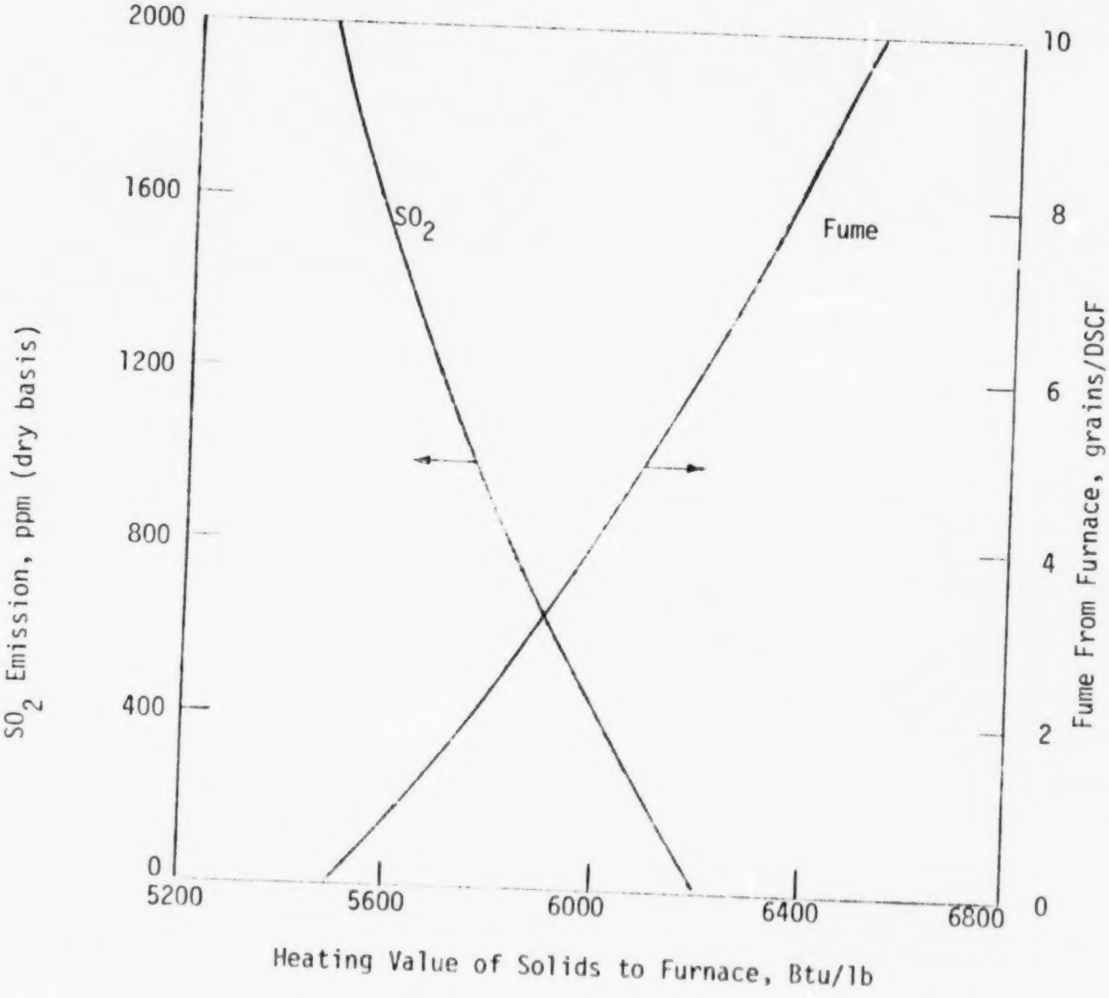


Figure 8-3

EFFECT OF TOTAL AIR SUPPLIED TO THE UNIT

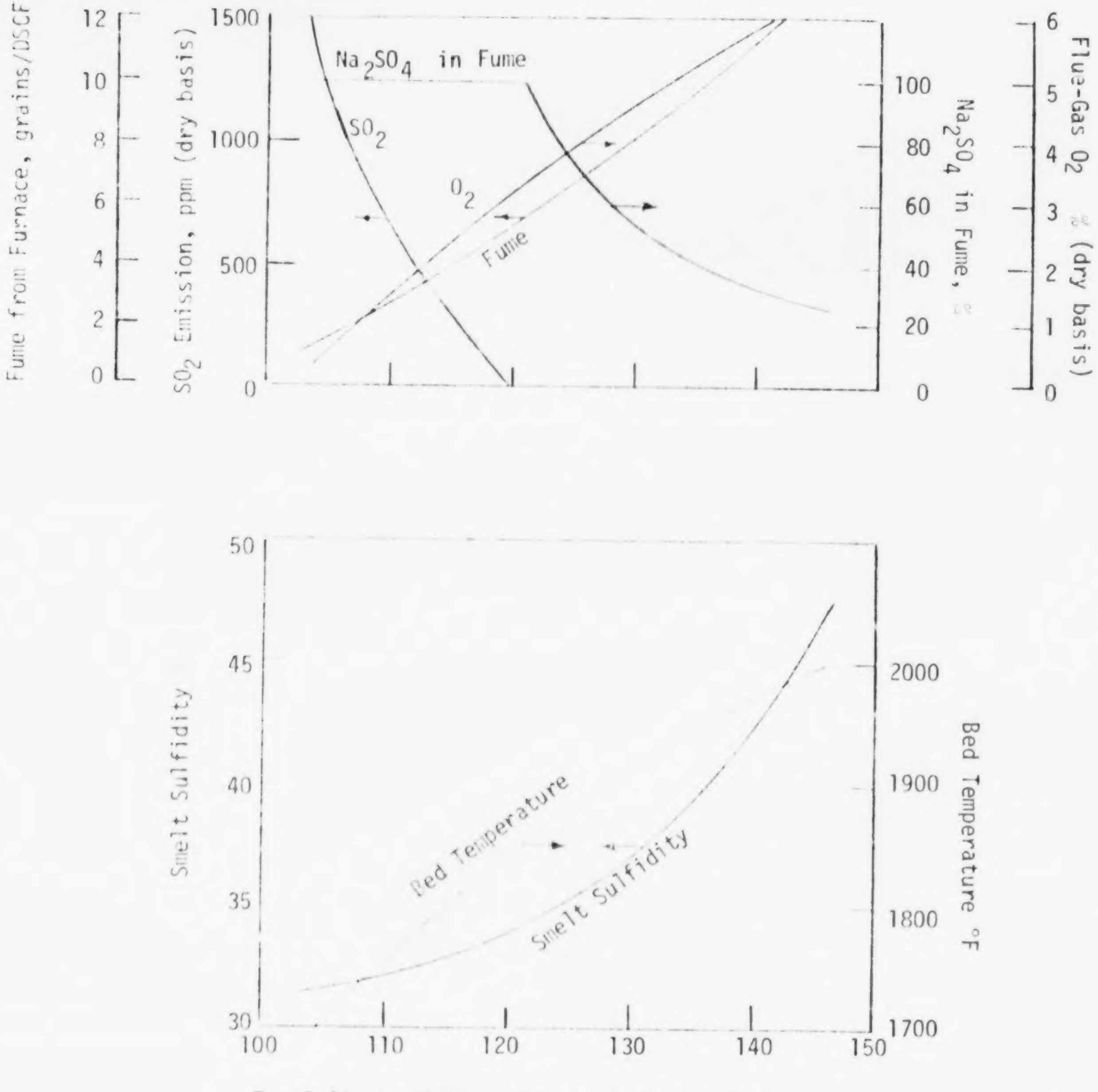


Figure 8-4

EFFECT OF PRIMARY AIR

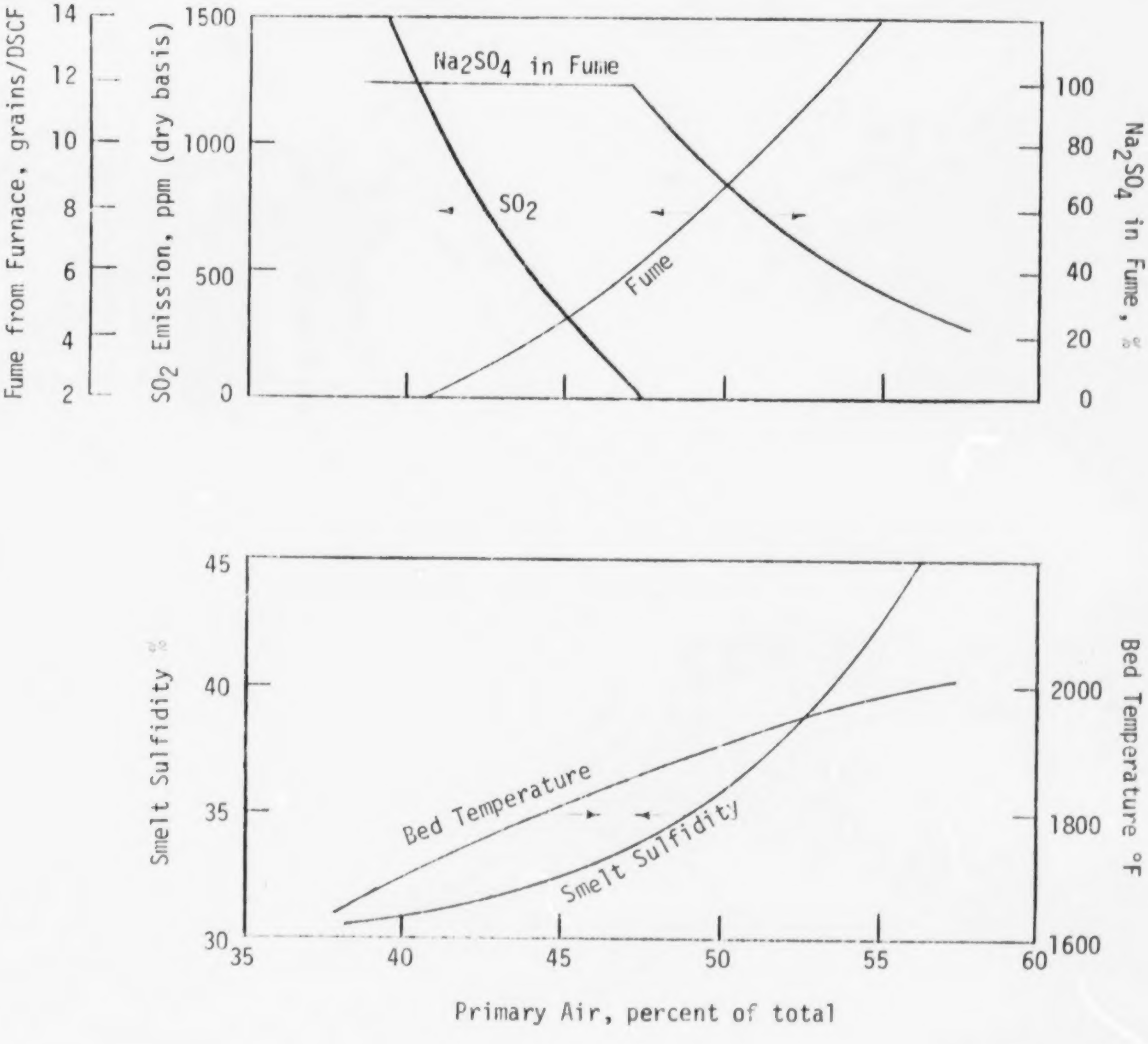


Figure 8-5

EFFECT OF PRIMARY AIR TEMPERATURE

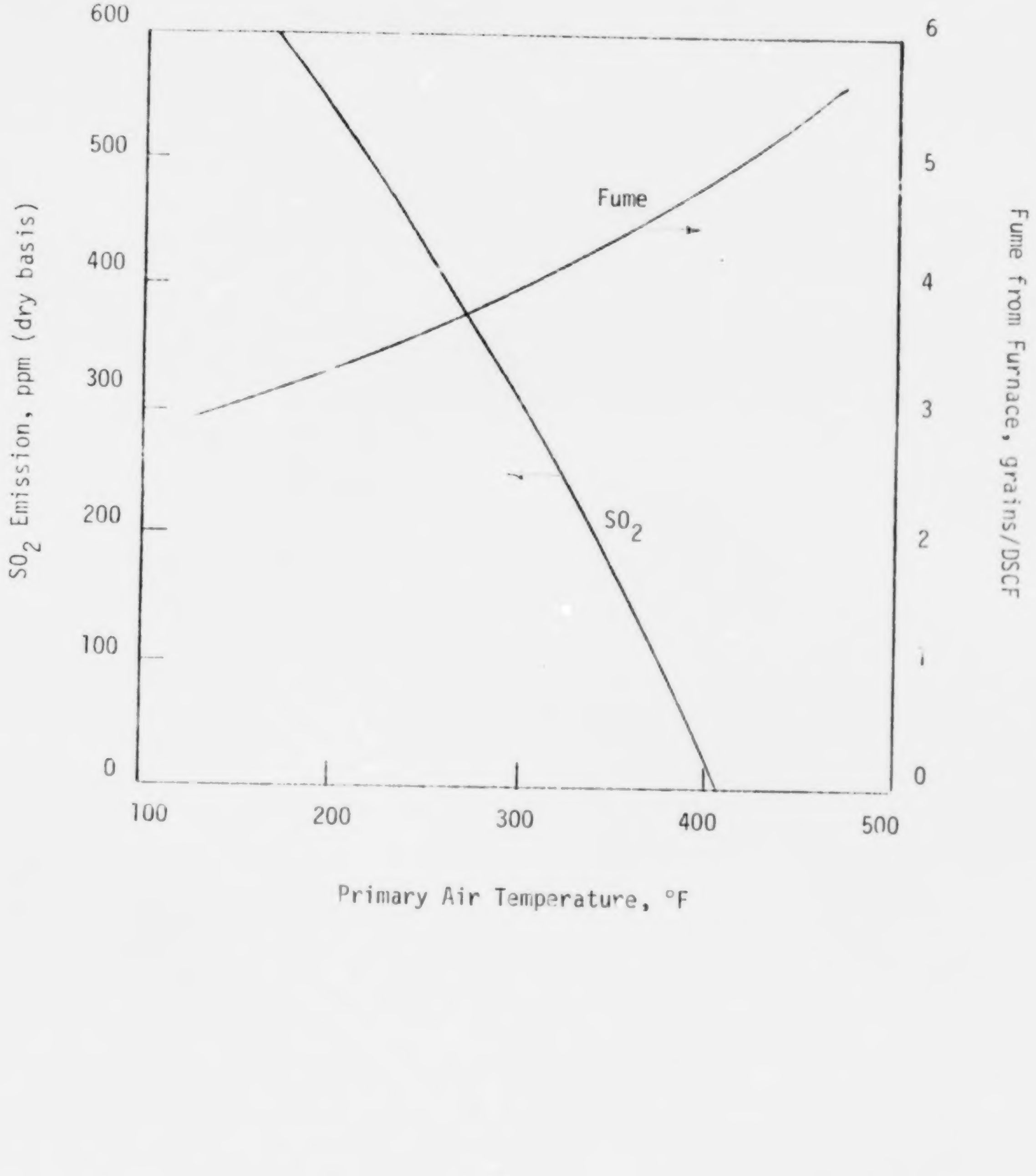


Figure 8-6

EFFECT OF SULFUR-SODIUM RATIO IN THE BLACK LIQUOR

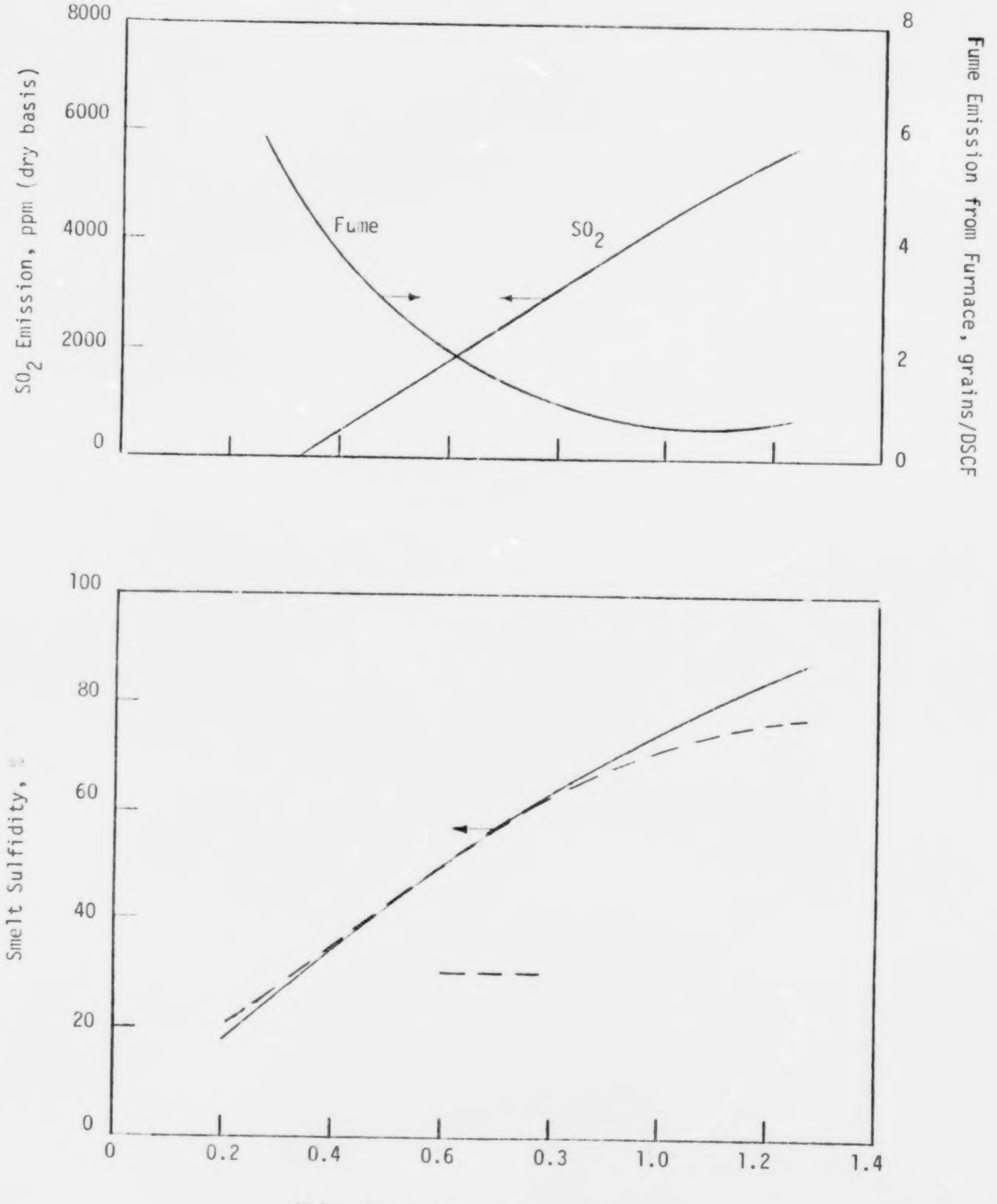
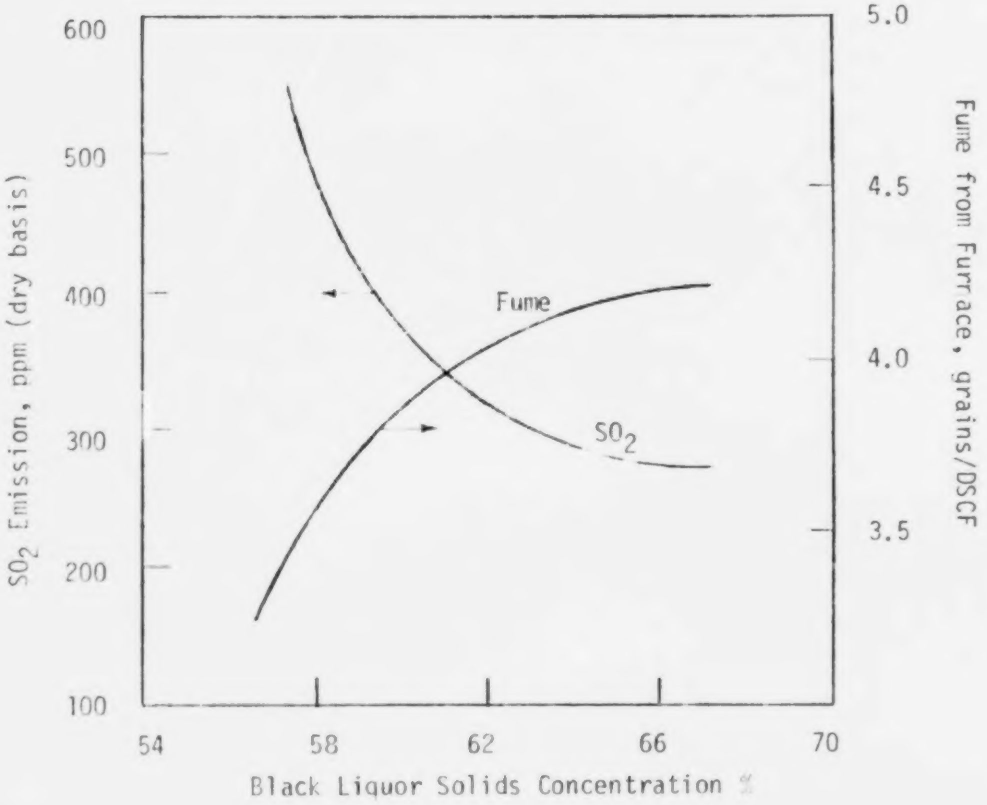


Figure 8-7

Effect of Black Liquor Solids Concentration



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APPENDIX

This appendix contains a series of graphical relationships, tables, and standard calculations which should be useful in assisting the FEO to estimate emission quantities. Insofar as process operations are concerned, the bulk of these data pertain to kraft pulping operations. Further in this regard, these data may only be used for estimating emission levels relative to the basis indicated.

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TABLE 1. FLUE GAS PARTICULATE CONCENTRATION AND EMISSION RATE RELATIONSHIPS FOR KRAFT RECOVERY FURNACES

Grains/SDCF	lbs/Ton Pulp	lbs/Hour (ONE TON/DAY MILL)
0.01	0.473	0.0197
0.02	0.946	0.0394
0.03	1.42	0.0591
0.04	1.89	0.0788
0.05	2.37	0.0985
0.06	2.84	0.118
0.07	3.31	0.138
0.08	3.78	0.158
0.09	4.26	0.177
0.10	4.73	0.197
0.20	9.46	0.394
0.40	18.9	0.788
0.50	23.7	0.985
0.60	28.4	1.182
0.80	37.8	1.58
1.00	47.3	1.97
2.00	94.6	3.94
4.00	189	7.88
6.00	284	11.8
8.00	378	15.8
10.00	473	19.7

Note: Interpolate for values not shown, or refer to Figures 1, 2 and 3.

TABLE 2. GAS CONCENTRATION AND SULFUR EMISSION RATE RELATIONSHIPS FOR KRAFT RECOVERY FURNACES

PPM by Volume	Pounds/Ton Pulp as Sulfur
1	0.0274
5	0.137
10	0.274
20	0.548
40	1.10
60	1.64
80	2.19
100	2.74
200	5.48
400	11.0
600	16.4
800	21.9
1000	27.4

One pound of Sulfur/Ton pulp = 36.4 PPM

TABLE 3. FLUE GAS PARTICULATE CONCENTRATION AND EMISSION RATE RELATIONSHIPS FOR LIME KILNS

Grains/SDCF	lbs/Ton	lbs/Hour (ONE TON/DAY MILL)
0.01	0.0822	0.00343
0.02	0.164	0.00686
0.03	0.247	0.0103
0.04	0.328	0.0137
0.05	0.411	0.0172
0.06	0.493	0.0209
0.07	0.575	0.0240
0.08	0.658	0.0274
0.09	0.740	0.0309
0.10	0.822	0.0343
0.20	1.64	0.0686
0.40	3.29	0.137
0.60	4.93	0.206
0.80	6.58	0.274
1.00	8.22	0.343
2.00	16.44	0.686
4.00	32.9	1.37
6.00	49.3	2.06
8.00	65.8	2.74
10.00	82.2	3.43
15.00	123	5.15
20.00	164	6.86

TABLE 4. FLUE GAS SULFUR CONCENTRATION AND SULFUR EMISSION RATE RELATIONSHIPS FOR LIME KILNS

PPM by Volume	Pounds/Ton Pulp as Sulfur
1	0.00476
5	0.0238
10	0.0476
20	0.0952
40	0.190
50	0.238
60	0.286
80	0.381
100	0.476
200	0.952
400	1.90
500	2.38
600	2.86
800	3.81
1000	4.76

One pound of Sulfur/Ton = 210 PPM.

TABLE 5. VENT GAS PARTICULATE CONCENTRATION AND EMISSION RATE RELATIONSHIPS FOR SMELT DISSOLVING TANKS

Grains/SDCF	lbs/Ton Pulp	lbs/Hour (ONE TON/DAY MILL)
0.01	0.0576	0.0024
0.02	0.115	0.0048
0.03	0.173	0.0072
0.04	0.230	0.0096
0.05	0.288	0.0120
0.06	0.346	0.0144
0.07	0.403	0.0168
0.08	0.461	0.0192
0.09	0.518	0.0216
0.10	0.576	0.0240
0.20	1.15	0.0480
0.40	2.30	0.0960
0.60	3.46	0.144
0.80	4.61	0.192
1.00	5.76	0.240
1.50	8.64	0.360
2.00	11.5	0.480

Gaseous Sulfur Emissions

Table 6 presents gaseous sulfur emission rates expressed as pounds of sulfur corresponding to concentrations in parts per million parts by volume dry gas. This vent gas has a mean moisture content of about 40% by volume. These relationships shown in Table #6 assume that the gaseous molecule contains only one atom of sulfur. An average value of 28 SDCFM/TPD was used in calculating emission rates. Figure 15 presents these data in graphical form.

TABLE 6. VENT GAS SULFUR CONCENTRATION AND EMISSION RATE RELATIONSHIPS FOR SMELT DISSOLVING TANKS

PPM by Volume	Pounds/Ton as Sulfur
1	0.0033
5	0.0167
10	0.0333
15	0.0500
20	0.0667
25	0.0834
50	0.167
75	0.250
100	0.333
200	0.667
500	1.67
700	2.33
1000	3.33

One pound of sulfur/ton = 300 PPM

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TABLE 7. SULFUR DIOXIDE CONCENTRATIONS IN POWER BOILER FLUE GAS AS A FUNCTION OF SULFUR CONTENT OF FUEL

Fuel Sulfur Content Percent	PPM SO_2 (v/v) - Coal			PPM SO_2 (v/v) - Oil	
	20% Excess Air	50% Excess Air	12% CO_2 Content	20% Excess Air	12% CO_2 Content
0.10	77	62	63	55	51
0.25	190	150	160	140	130
0.50	380	300	310	280	260
1.00	770	610	620	550	510
1.50	1150	920	940	830	770
2.00	1530	1210	1240	1100	1030
2.50	1910	1510	1550	1380	1280
3.00	2300	1810	1780	1660	1540
3.50	2680	2110	2180	1930	1800
4.00	3060	2420	2490	2210	2060
5.00	3830	3020	3100	2760	2580

Note: Interpolate for values not shown.

TABLE 7
(continued)

1. Coal

Heat value - 13,000 BTU/pound

Carbon Content - 72.8%

Theoretical combustion air =

7.6 pounds/10,000 BTU

Theoretical air = 9.9 pounds/pound of coal

20% Excess Air = 11.85 pounds air/pound of coal

At 70°F, 1 Atm., 11.85 pounds of air =

158 ft^3 dry air

1 pound of coal of 1% sulfur content produces

0.121 ft^3 of SO_2 assuming 100% combustion and no sulfur discharged with ash

PPM SO_2 (1% sulfur) = $0.121/158 \times 10^6$ =

765 PPM

Pounds of SO_2 produced =

$$(2)\ \frac{(\%\ \text{Sulfur})\ (\text{Pounds of Coal})}{100}$$

2. Oil (No. 6 or "Bunker C")

Heat value - 18,500 BTU/pound

Carbon Content = 88.4%

Theoretical combustion air =

7.46 pounds/10,000 BTU

Theoretical air = 13.80 pounds/pound of oil

20% excess air - 16.5 pounds/pound of oil

At 70°F, 1 Atm., 16.55 pounds of air =

TABLE 7
(continued)

220 ft^3 dry air.

1 pound of oil at 1% sulfur produces

0.121 ft^3 of SO_2 assuming 100% combustion.

PPM SO_2 (1% Sulfur) = $0.121/220 \times 10^6$ =

552 PPM

Pounds of SO_2 produced =

$$\frac{(2)\ (\%\ \text{Sulfur})\ (\text{Pounds of Oil})}{100.0}$$

TABLE 8
CONVERSION OF DUST LOADING IN BOILER FLUE GAS FROM GR./SCF TO LB./MM BTU OF HEAT INPUT AND VICE VERSA

Federal guidelines for particulate emission rates are expressed in lb./MM BTU of heat input while many state regulations are expressed in gr./SCF. The following formulas and curves can be used to relate these two values.

1. COAL FIRED BOILER:

Step 1: If percent O_2 in flue gas is not known, determine percent O_2 from Figure 1 by assuming percent excess air or percent CO_2. Generally one of these three quantities are known.

Step 2: Determine multiplication factor A_1 from Figure 2.

Step 3: Determine multiplication factor B_1 from Figure 3.

Step 4: Calculate #/MM BTU from formula below:

$$\text{Lb/MM BTU} = (\text{Gr/SCF})\ (A_1)\ (B_1) \text{ or}$$

$$\text{Gr/SCF} = \frac{\text{Lb}}{\text{MM BTU}} \quad \frac{1}{(A_1)} \times \frac{1}{(B_1)}$$

2. OIL FIRED BOILER:

Step 1: If percent O_2 in flue gas is not known, determine percent O_2 from Figure 1 by assuming percent excess air or percent CO_2. Generally one of these three quantities are known.

Step 2: Determine multiplication factor A_2 from Figure 4.

Step 3: Calculate #/MM BTU from formula below:

$$\text{Lb/MM BTU} = (\text{Gr/SCF}) \times (A_2) \text{ or}$$

$$\text{Gr/SCF} = \text{Lb/MM BTU} \times \left(\frac{1}{A_2}\right)$$

3. WOOD BARK OR BAGASSE FIRED BOILER:

Step 1: If percent O_2 in flue gas is not known, determine percent O_2 from Figure 1 by assuming percent excess air or percent CO_2. Generally one of these three quantities are known.

Step 2: Determine multiplication factor A_3 from Figure 5.

Step 3: Determine multiplication factor B_3 from Figure 6.

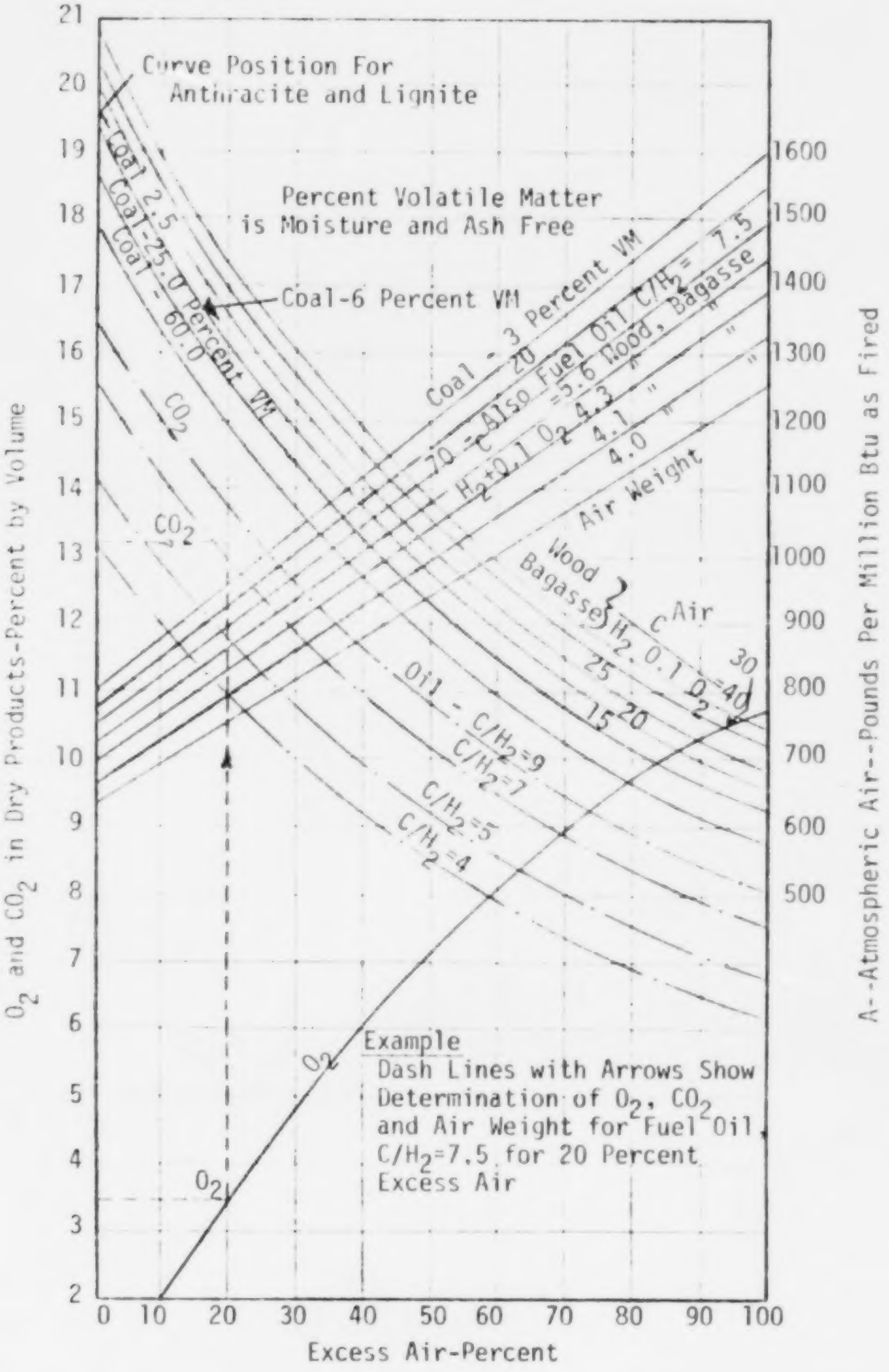
Step 4: Calculate #/MM BTU from formula below:

$$\text{Lb/MM BTU} = (\text{Gr/SCF})\ (A_3)\ (B_3) \text{ or}$$

$$\text{Gr/SCF} = \text{Lb/MM BTU}\ \frac{1}{(A_3)}\ \frac{1}{(B_3)}$$

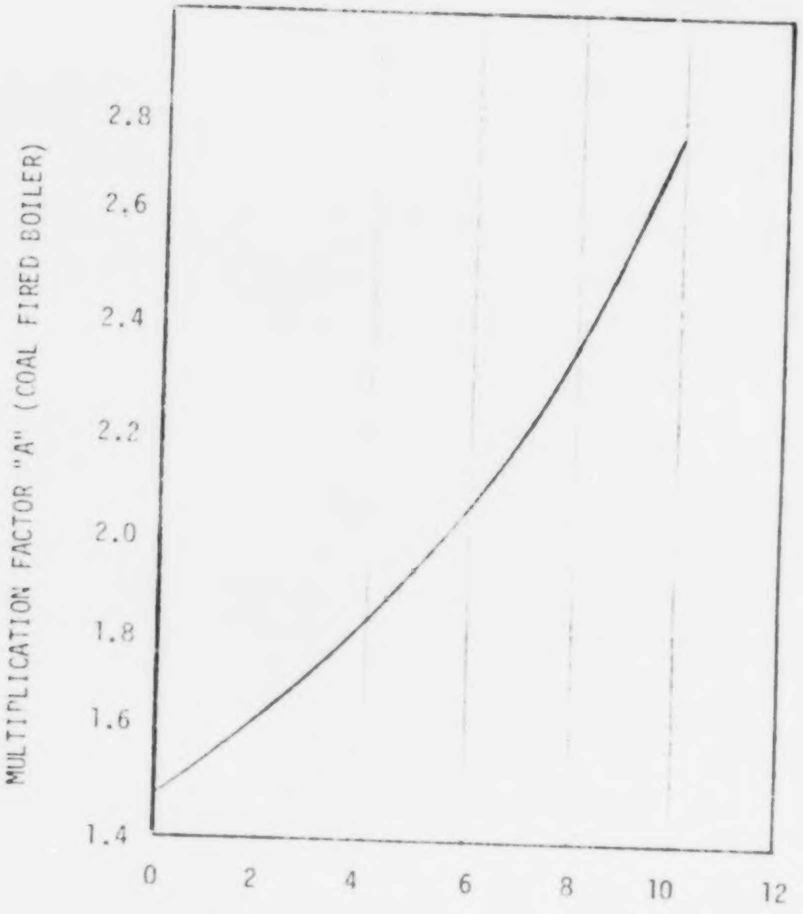
Results from the above calculations should be accurate within five percent of the true answer. Naturally, some generalization had to be made in simplifying the above calculation procedures which explain this accuracy range. Average values were utilized for the approximate analysis of the fuel in deriving the multiplication factor (A). Likewise a heat value was assumed for the generated steam of 1050 BTU/Lb. The multiplication factor (A) originates from thermodynamic combustion calculations and are compiled on a strictly theoretical level. Boiler efficiency does not enter into the above calculations and therefore only minimum assumptions must be made. Generally, either the percent oxygen in the flue gas, the percent carbon dioxide in the flue gas or the excess air is known, so it was decided that this would be a good starting point for the above computations. For oil and coal fired boilers the excess air would generally be in the neighborhood of thirty percent while for wood waste fired boilers this value might be as high as fifty percent. Notice that the family of curves for the coal fired boiler in Figure 1 varies with percent volatile matter.

Table 8
Figure 1



Example
Dash Lines with Arrows Show Determination of O_2, CO_2 and Air Weight for Fuel Oil, C/H_2=7.5 for 20 Percent Excess Air

Table 8

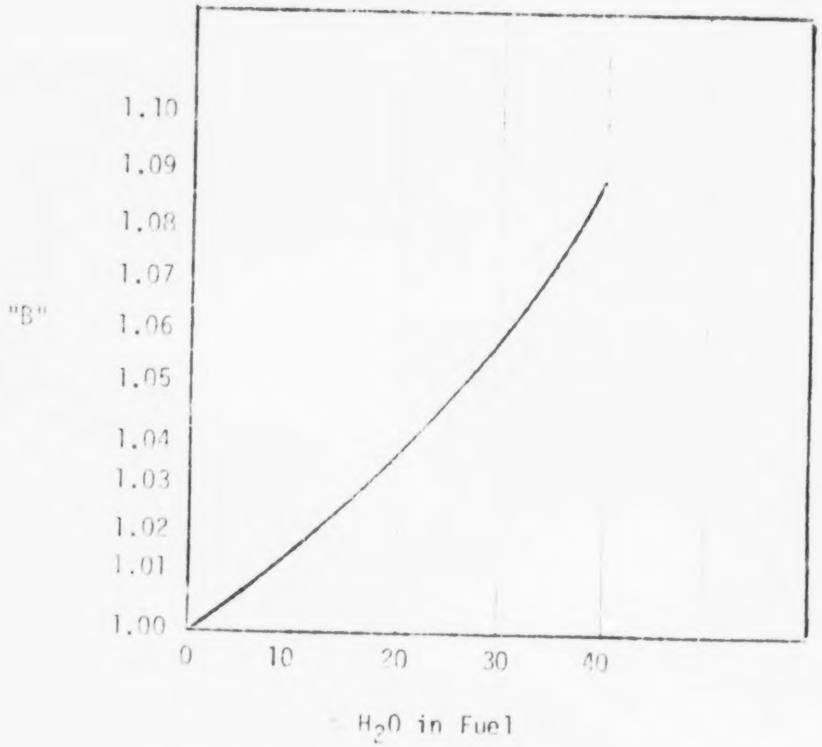


% Oxygen in Flue Gas

MULTIPLICATION FACTOR "A" FOR COAL FIRED BOILER

Figure 2

Table 8



MULTIPLICATION FACTOR "B" FOR COAL FIRED BOILER

Figure 3.

Table 8

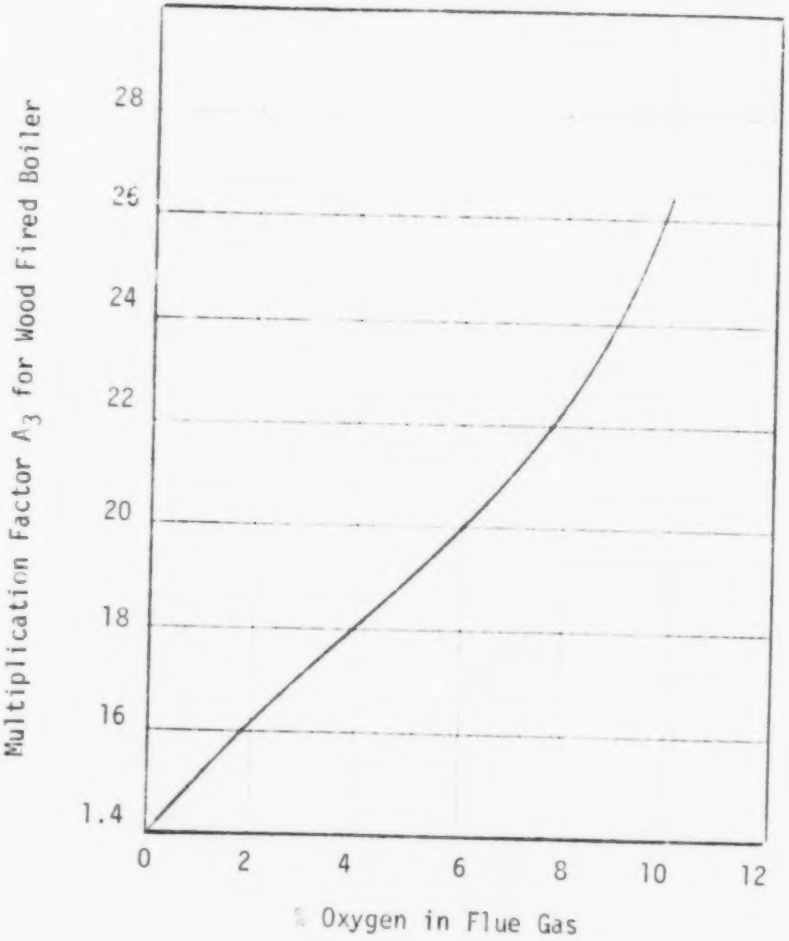


Figure 5

MULTIPLICATION FACTOR A_3 FOR WOOD FIRED BOILER

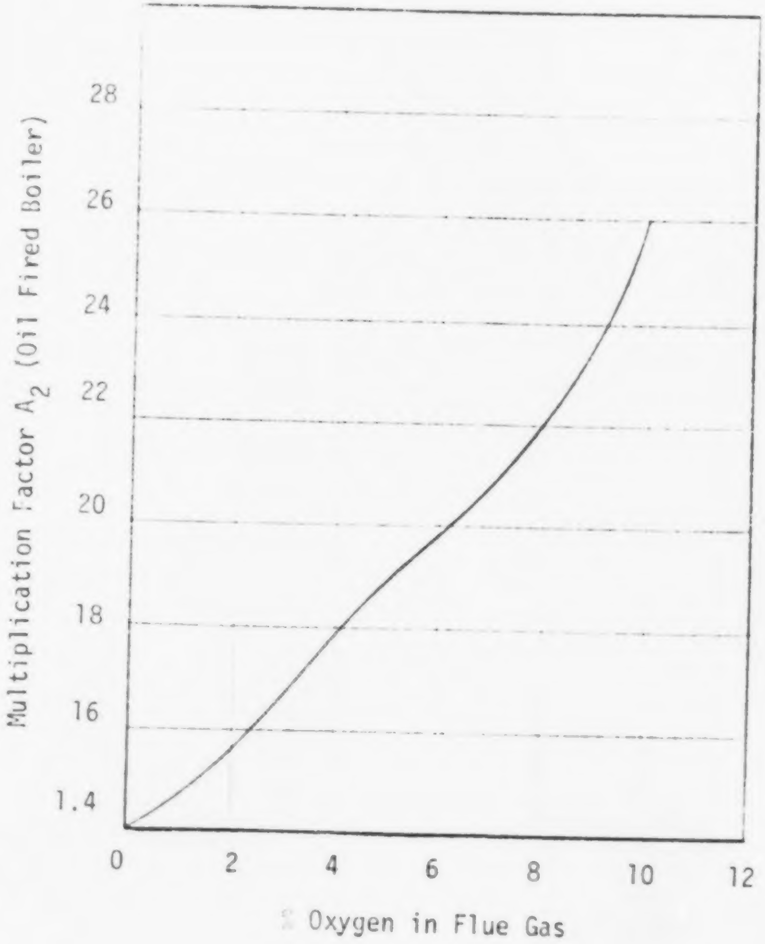


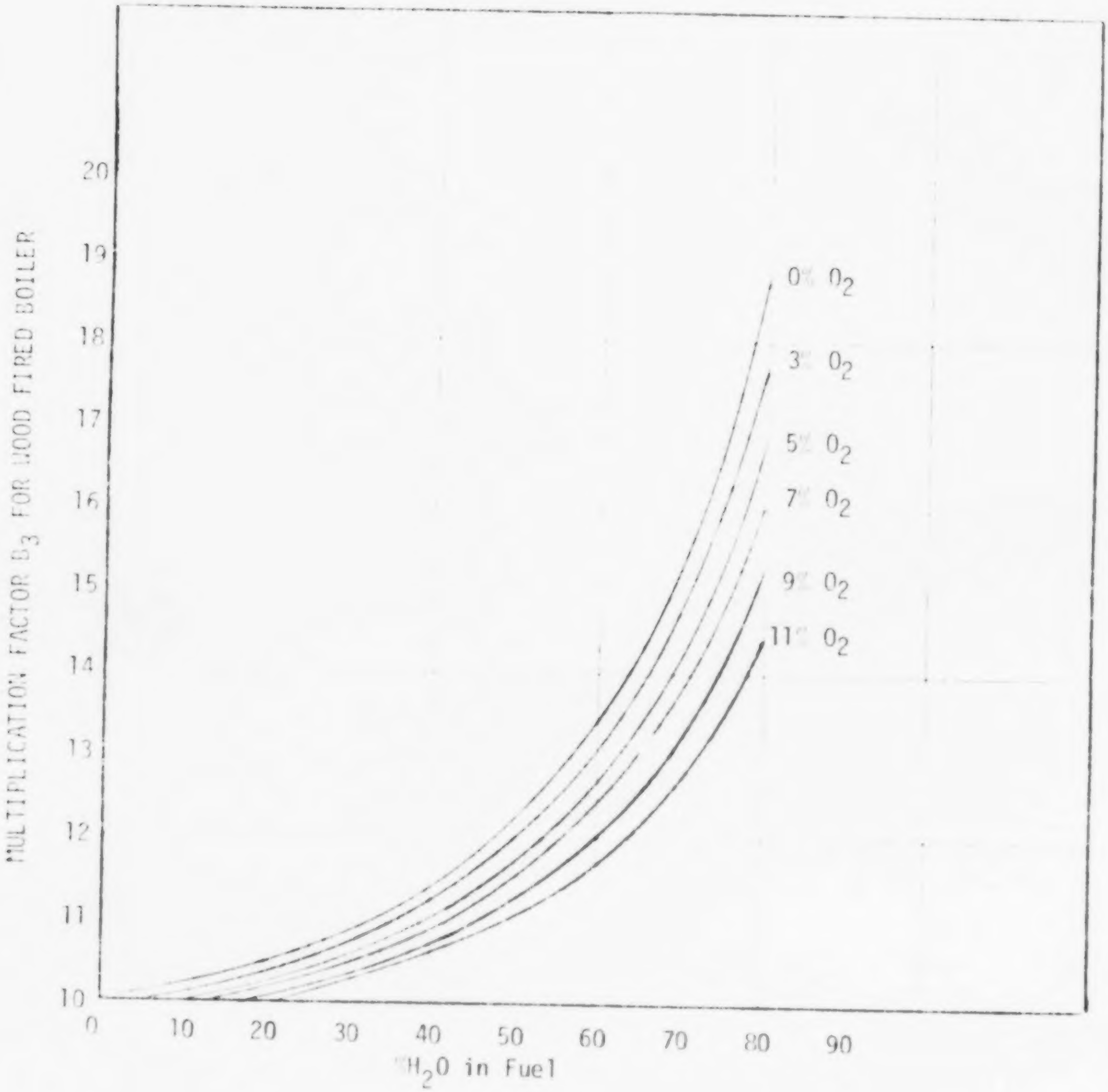
Figure 4

MULTIPLICATION FACTOR A_2 FOR OIL FIRED BOILER

TABLE 8

(continued)

Factor F_W



Multiplication Factor B_3 For Wood Fired Boiler
Figure 6

FOR KRAFT RECOVERY FURNACES

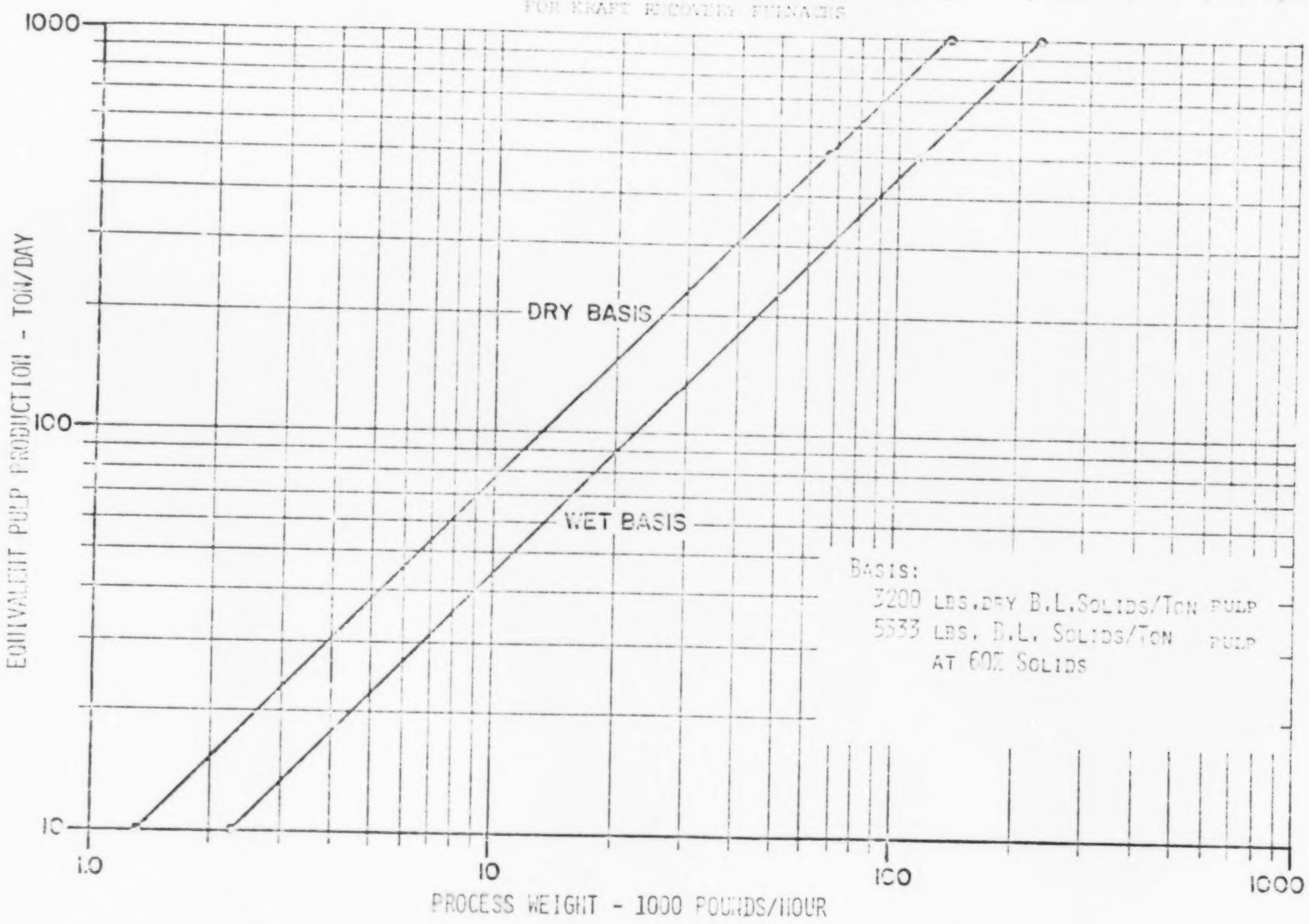
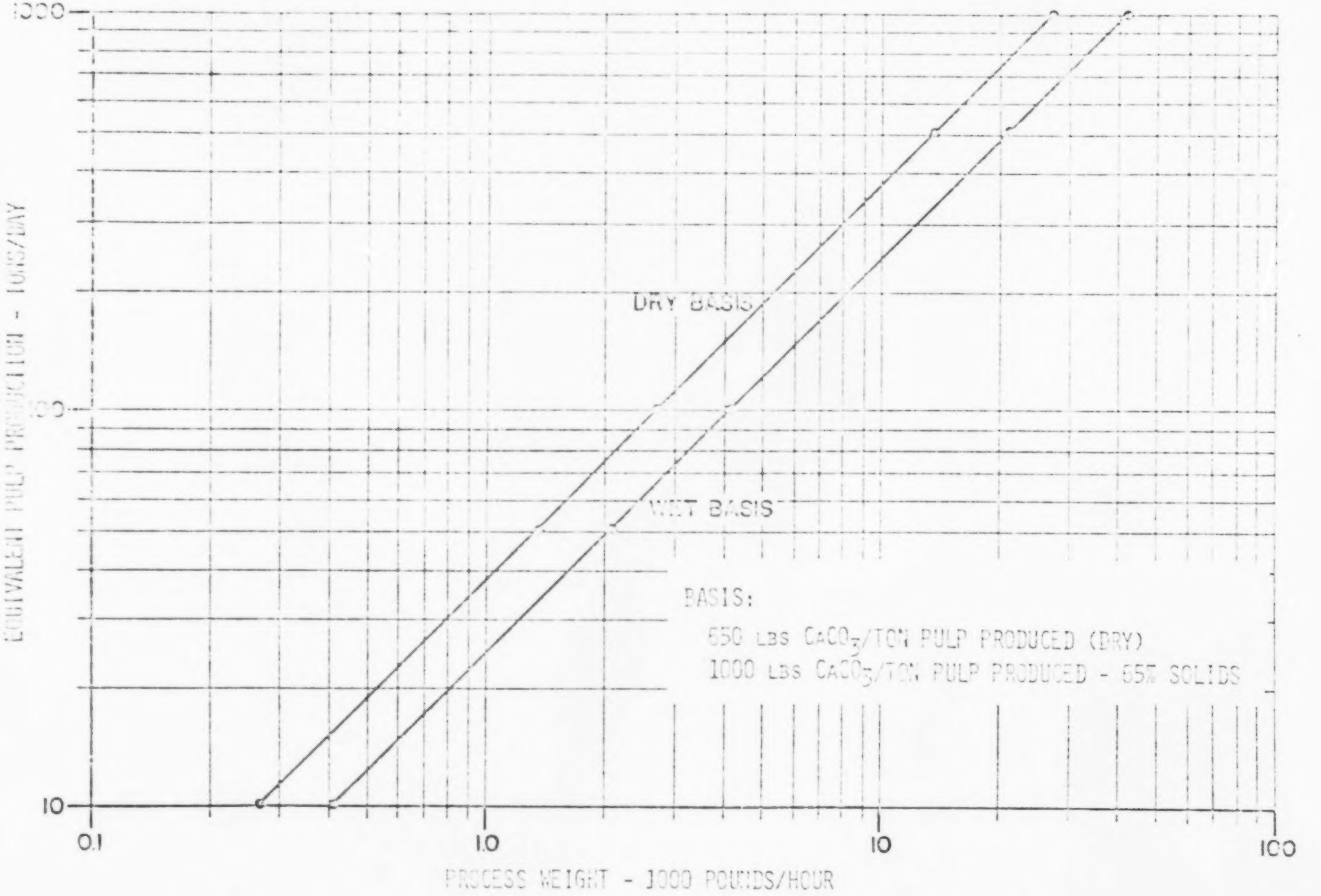


FIGURE 2. PROCESS WEIGHT AND EQUIVALENT PULP PRODUCTION RELATIONSHIPS FOR LIME KILNS



BASIS:

650 LBS $CaCO_3$/TON PULP PRODUCED (DRY)

1000 LBS $CaCO_3$/TON PULP PRODUCED - 65% SOLIDS

[illegible]

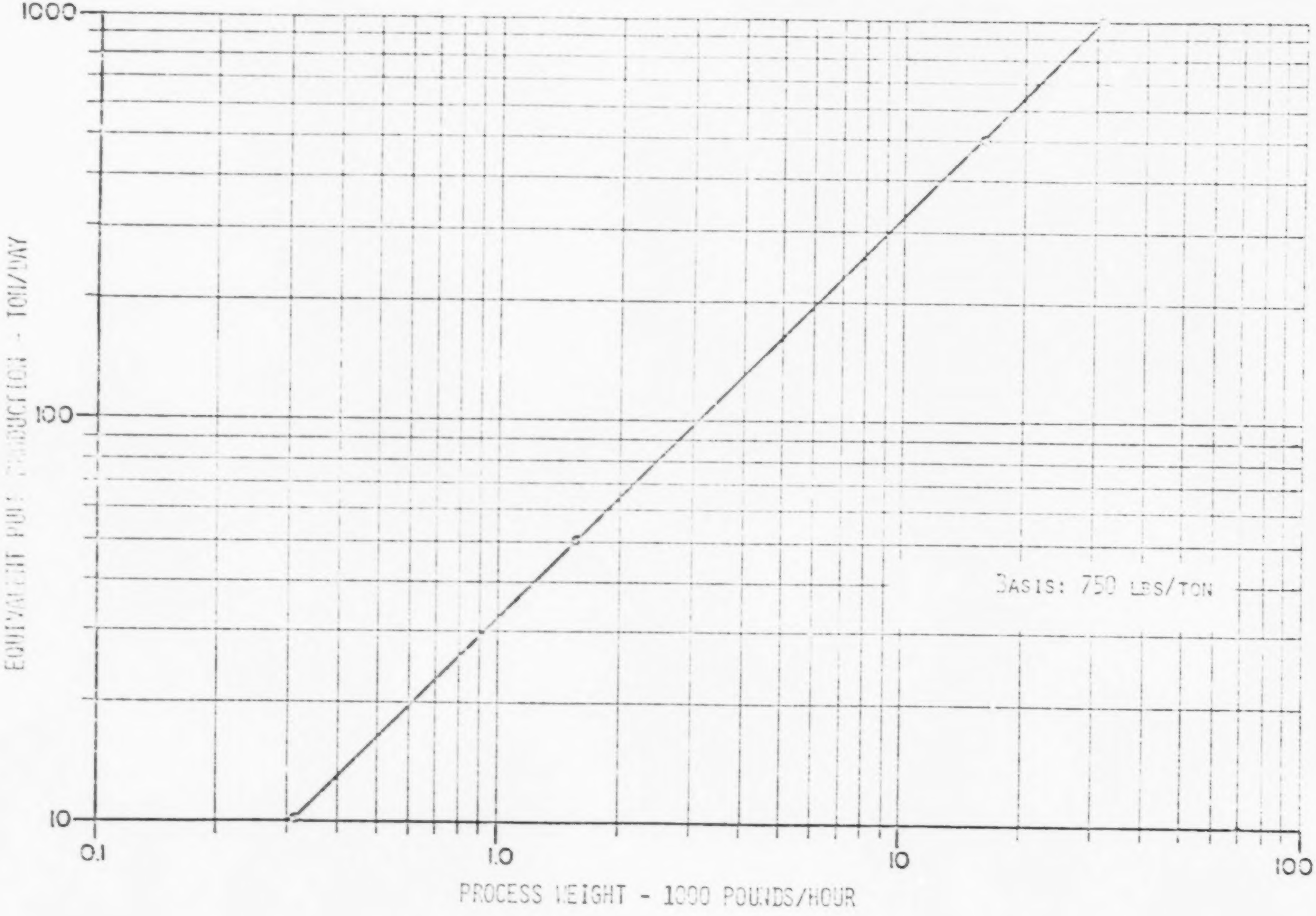

1000
100
10
0.1
1.0
10
100
EQUIVALENT PULP PRODUCTION - TON/DAY
PROCESS WEIGHT - 1000 POUNDS/HOUR
BASIS: 750 LBS/TON

FIGURE 4. PARTICULATE EMISSION RATE PER UNIT OF PULP PRODUCTION AS FUNCTION OF CONCENTRATION IN KRAFT RECOVERY FURNACE FLUE GAS

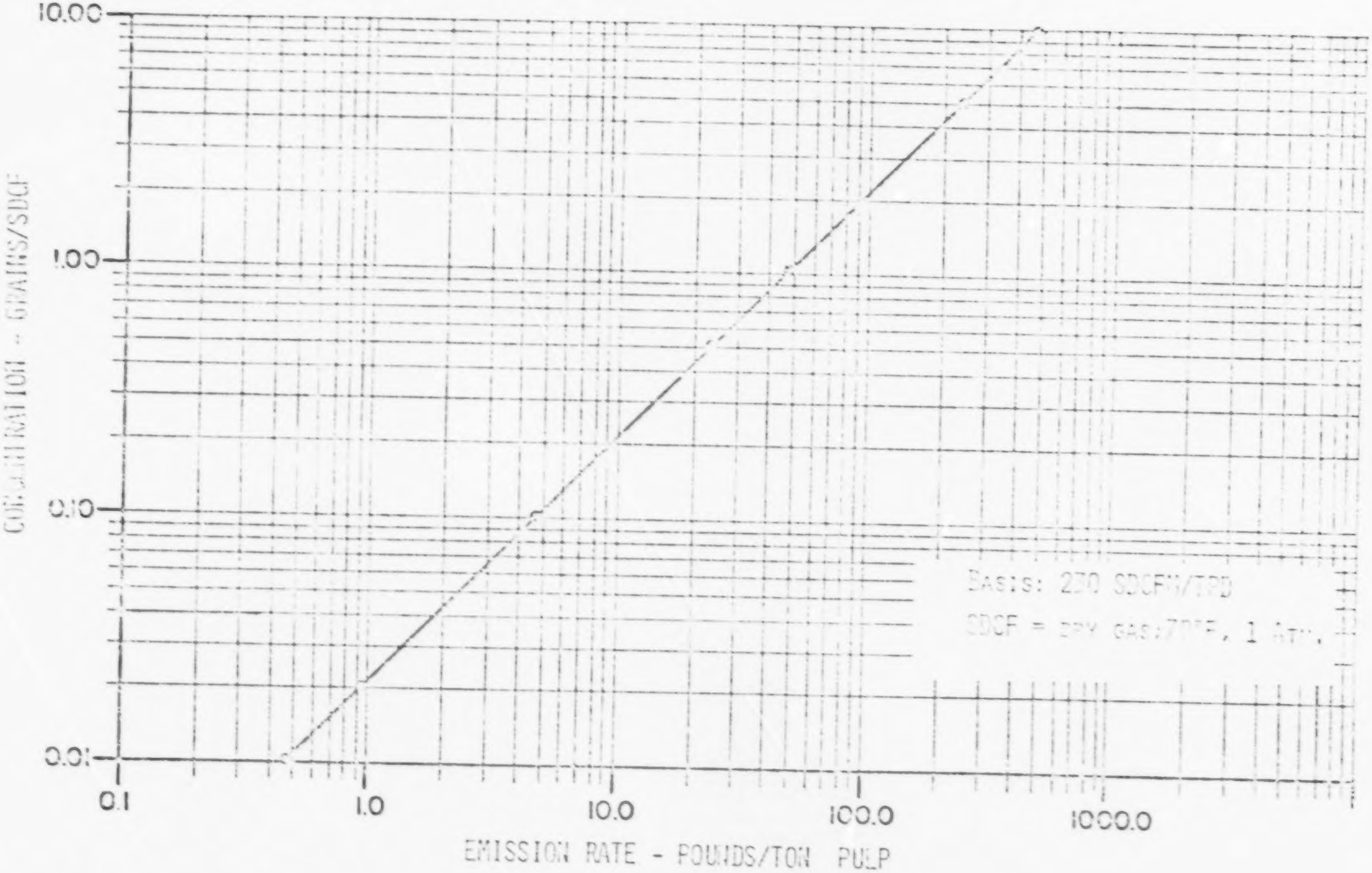


FIGURE 5. EMISSION RATE IN UNIT TIME AS FUNCTION OF CONCENTRATION IN KRAFT RECOVERY FURNACE FLUE GAS

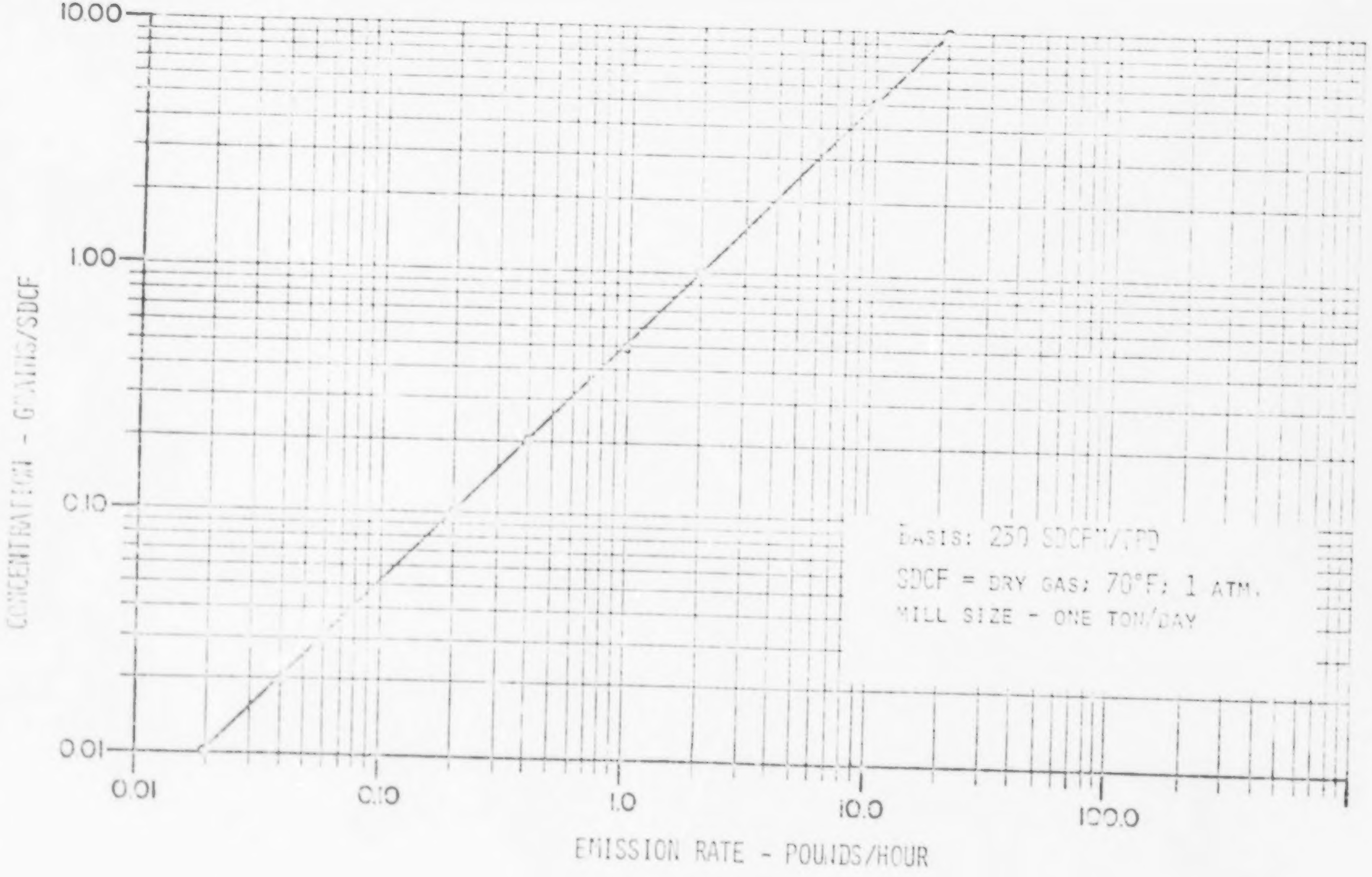


FIGURE 6. PARTICULATE EMISSION RATES AS A FUNCTION OF EQUIVALENT PULP PRODUCTION AND CONCENTRATION FOR KRAFT RECOVERY FURNACES

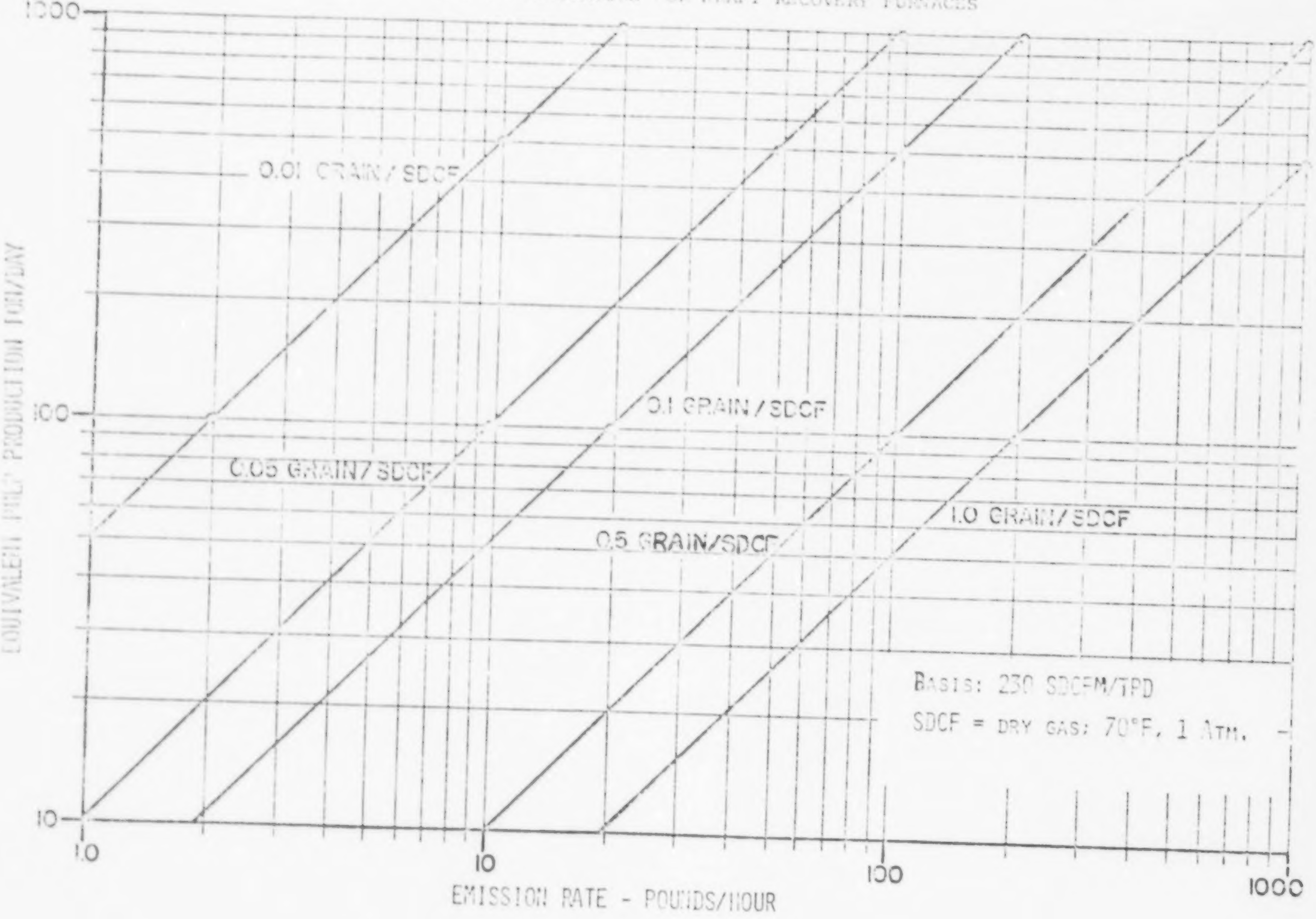


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FIGURE 7. GAS CONCENTRATION AND SULFUR EMISSION RATE RELATIONSHIPS FOR KRAFT RECOVERY FURNACES

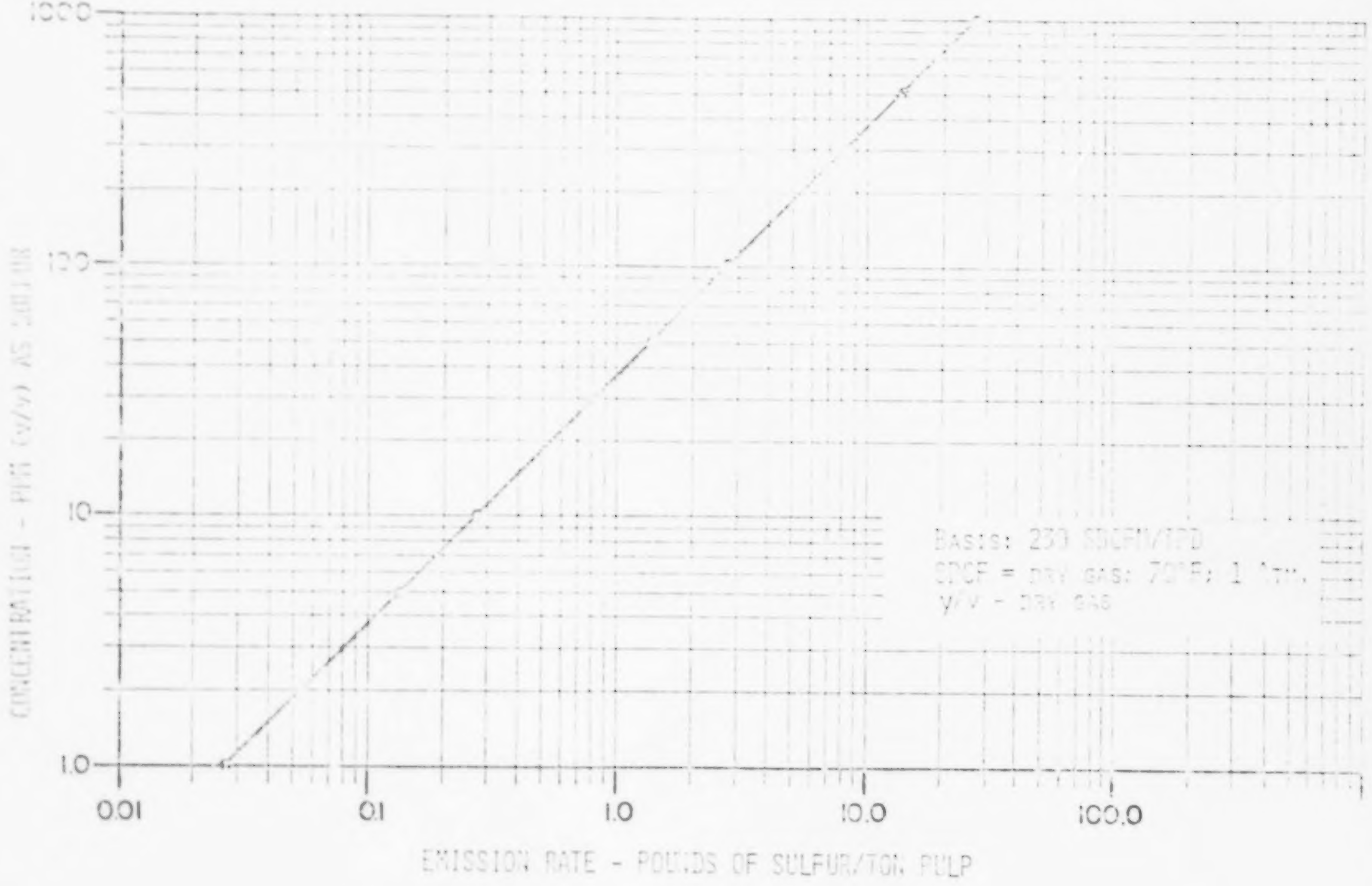
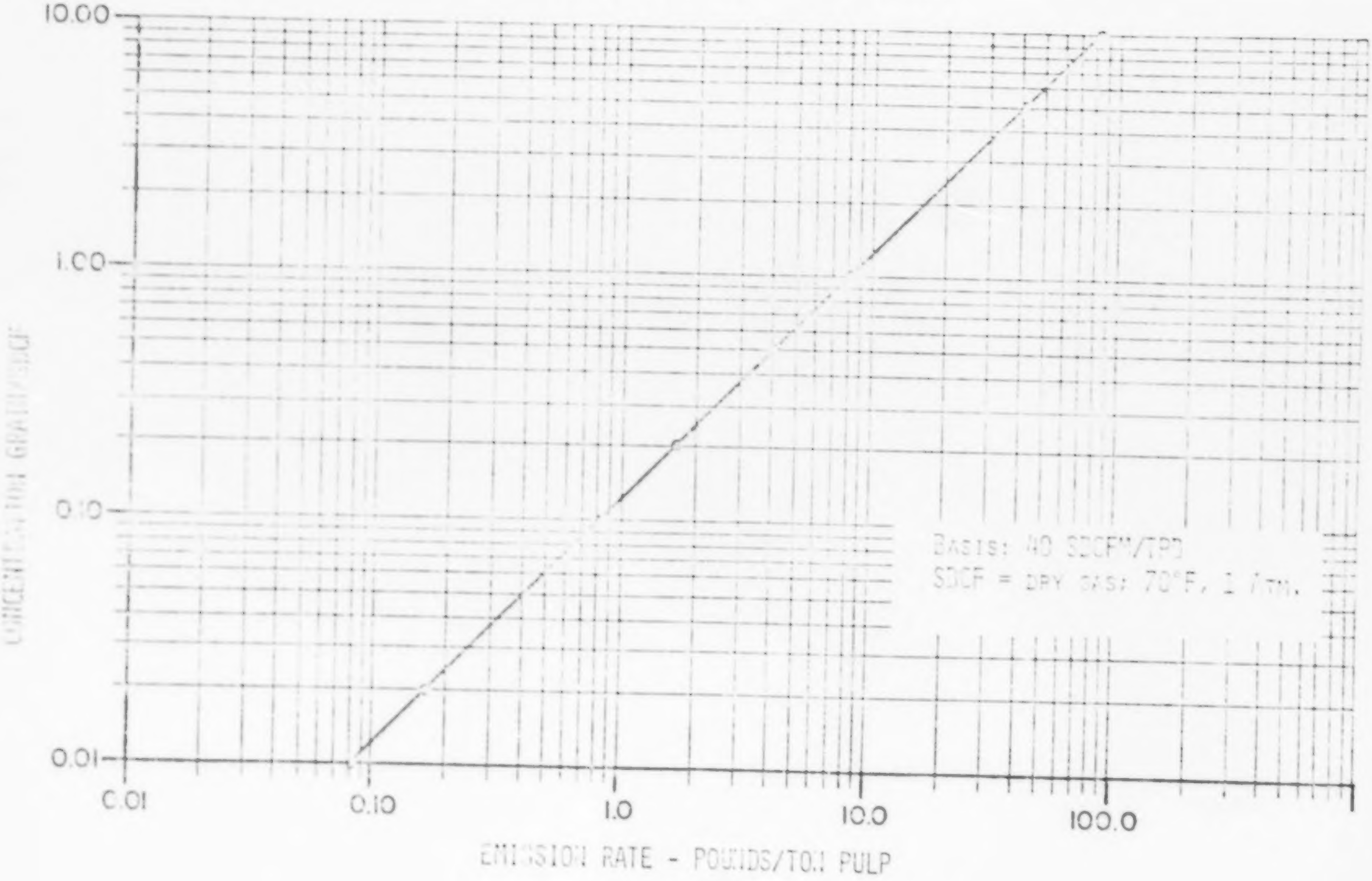


FIGURE 8. PARTICULATE EMISSION RATE PER UNIT OF PULP PRODUCTION AS FUNCTION OF CONCENTRATION IN LIME KILN FLUE GAS



[illegible] EMISSION RATE IN [illegible] FUNCTION OF CONCENTRATION
IN [illegible] FLUE GAS

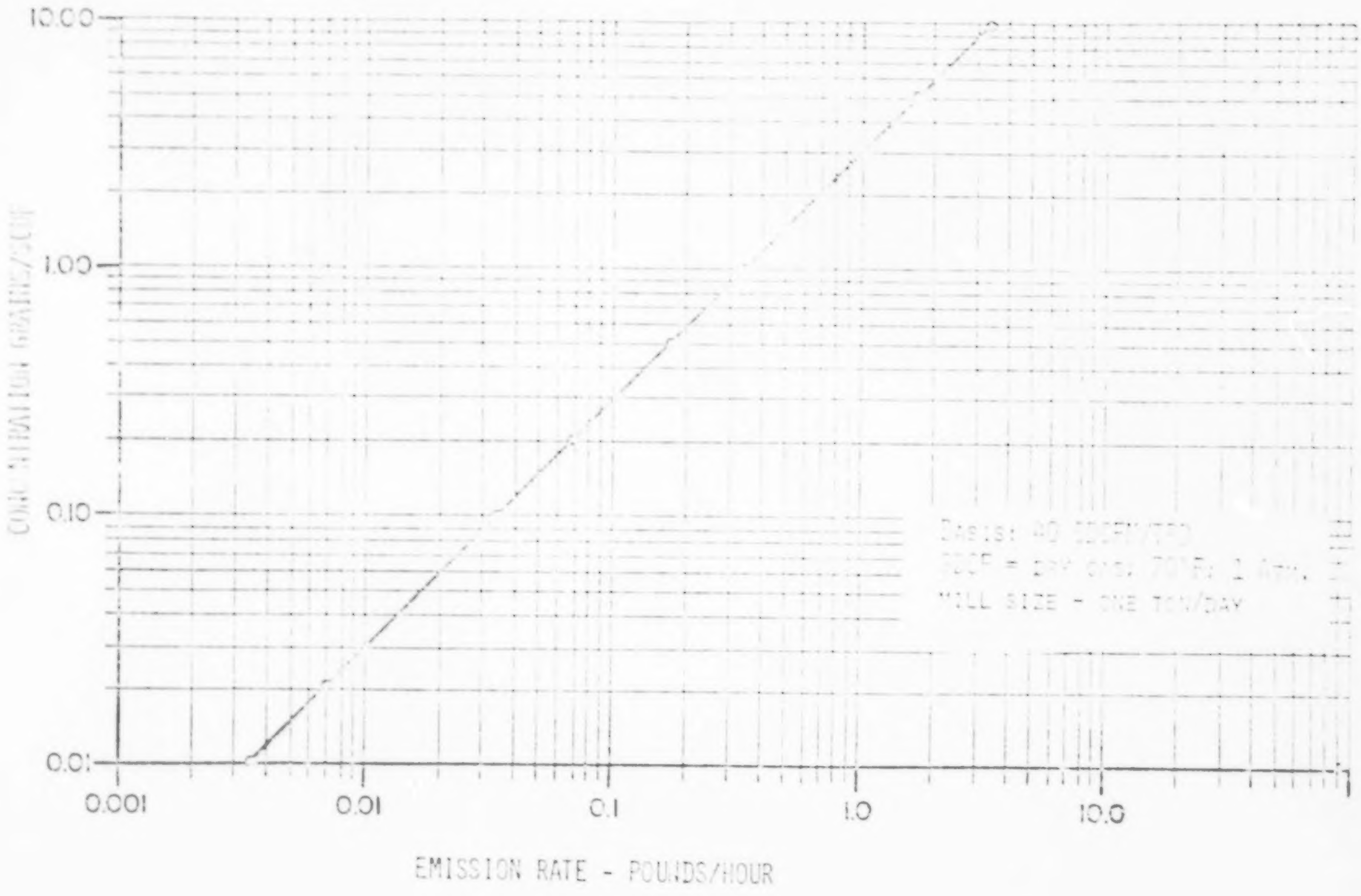


FIGURE 10. PARTICULATE EMISSION RATE AS FUNCTION OF EQUIVALENT PULP PRODUCTION AND CONCENTRATION FOR LIME KILNS

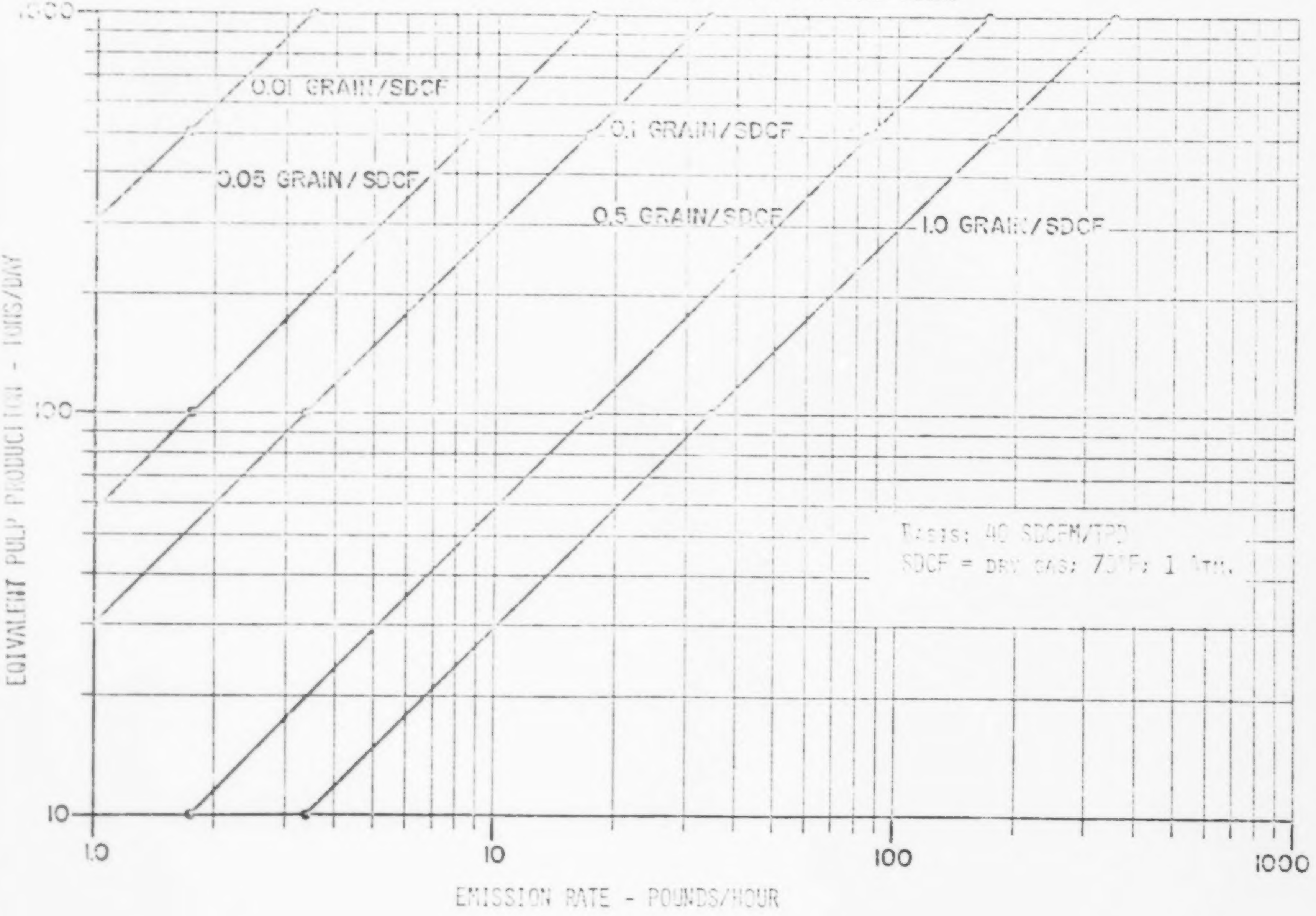


FIGURE 11. FLUE GAS CONCENTRATION AND SULFUR EMISSION RATE RELATIONSHIPS FOR LIME KILNS

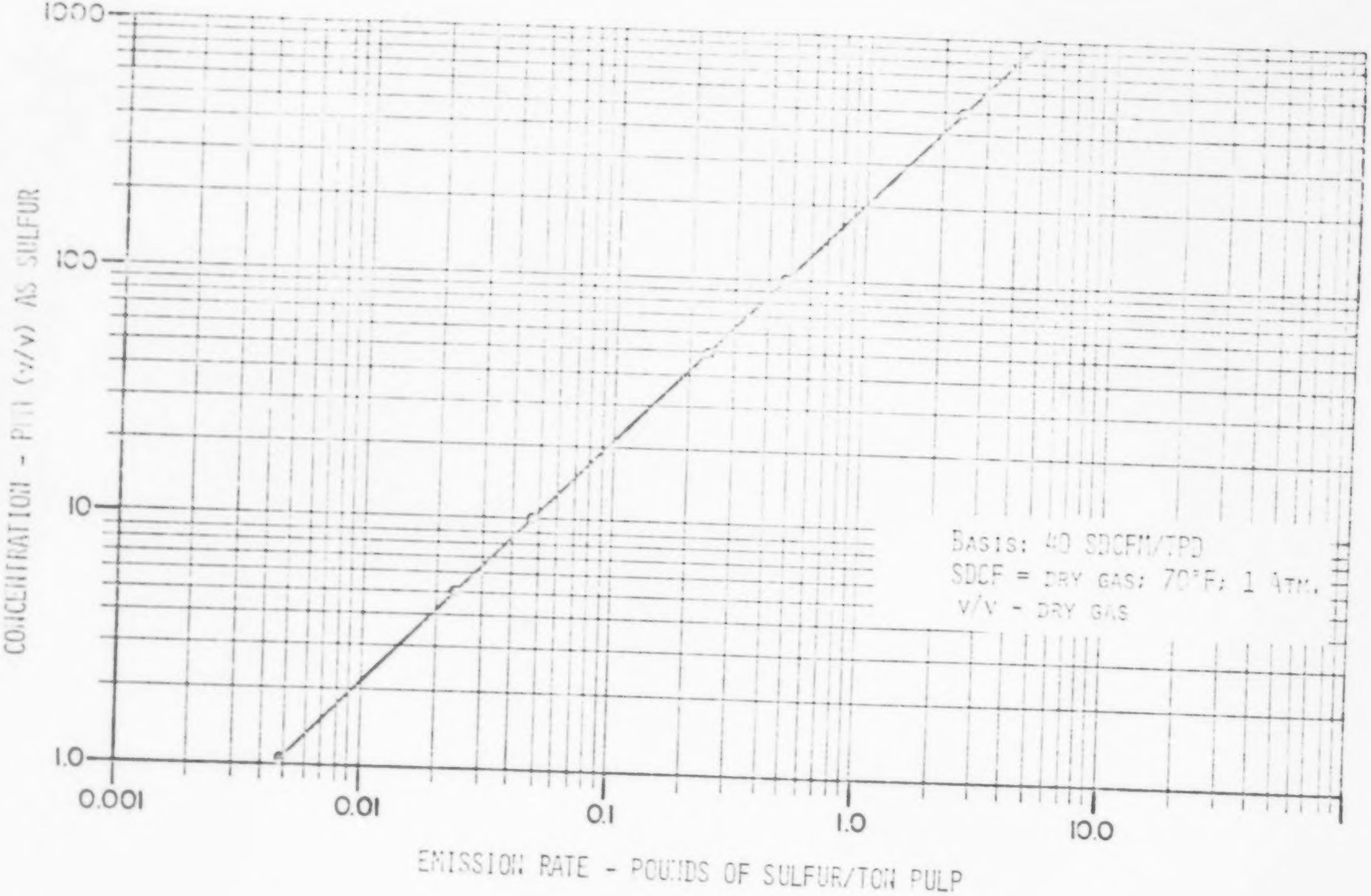


FIGURE 12. PARTICULATE EMISSION RATE PER UNIT OF PULP PRODUCTION AS FUNCTION OF CONCENTRATION IN SMELT DISSOLVING TANK VENT GAS

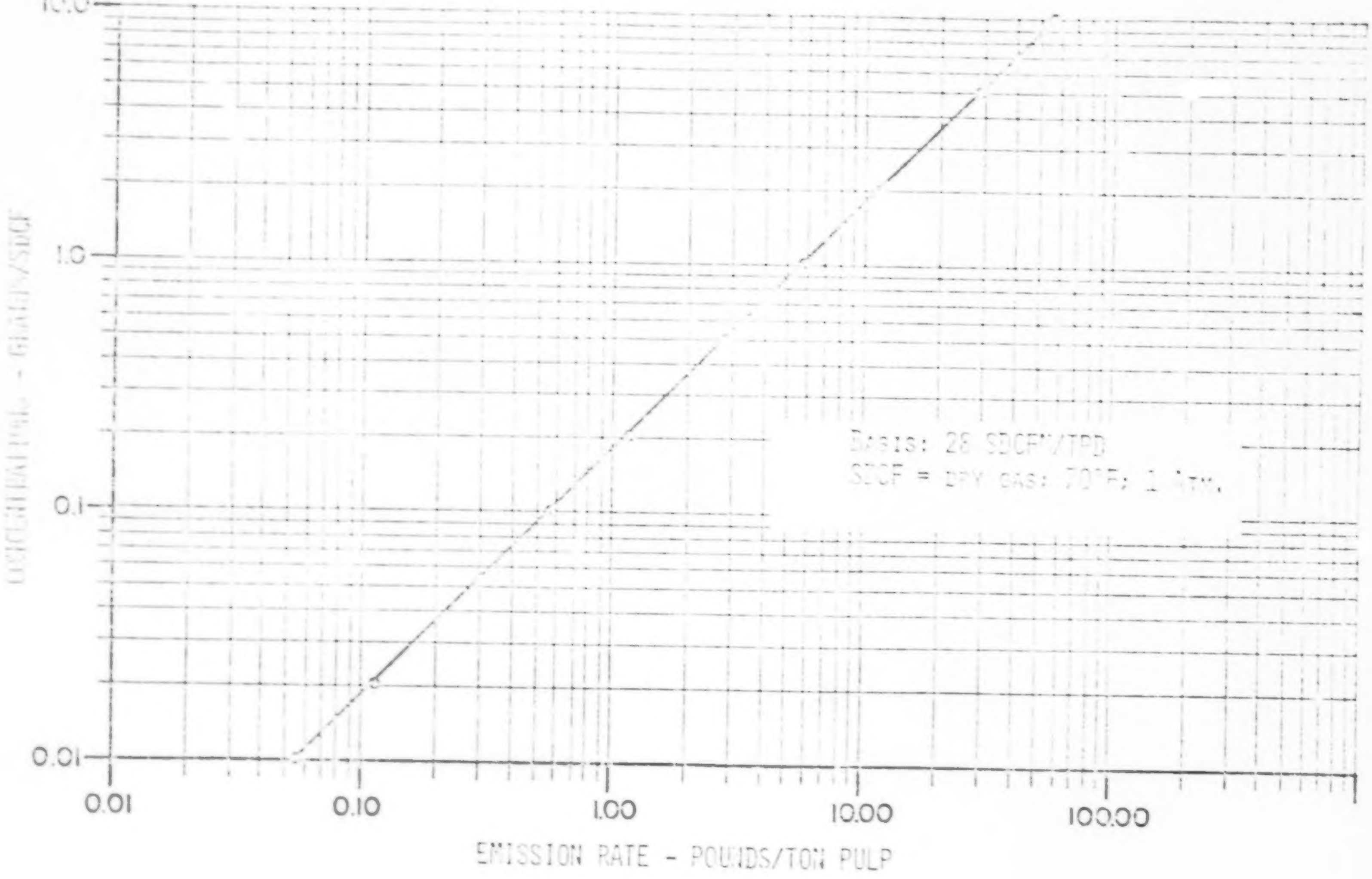


FIGURE 13. PARTICULATE EMISSION RATE IN UNIT TIME AS FUNCTION OF CONCENTRATION IN SMELT DISSOLVING TANK VENT GAS

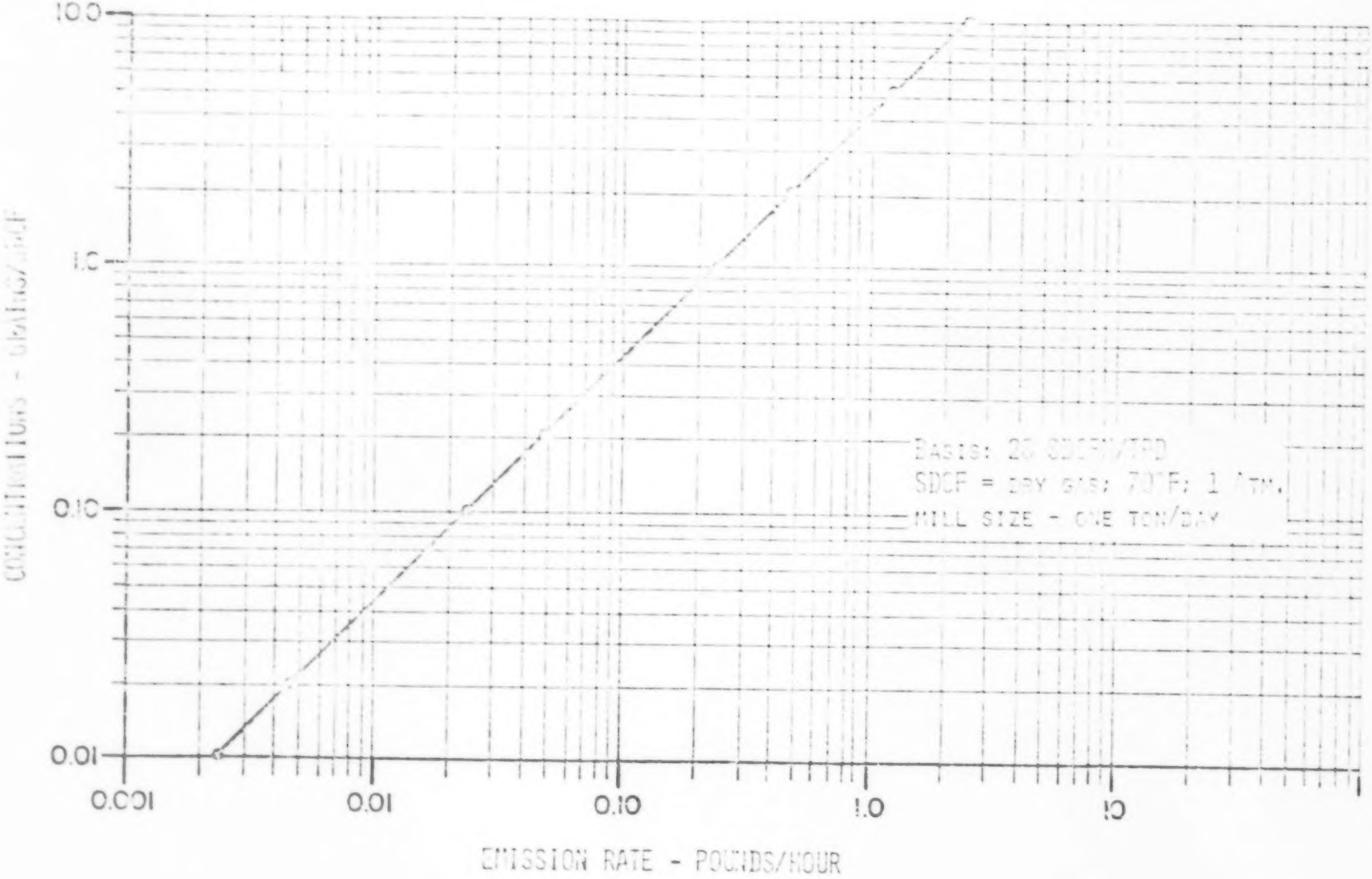


FIGURE 14. PARTICULATE EMISSION RATE AS FUNCTION OF EQUIVALENT PULP PRODUCTION AND CONCENTRATION FOR SMELT DISSOLVING TANK VENTS

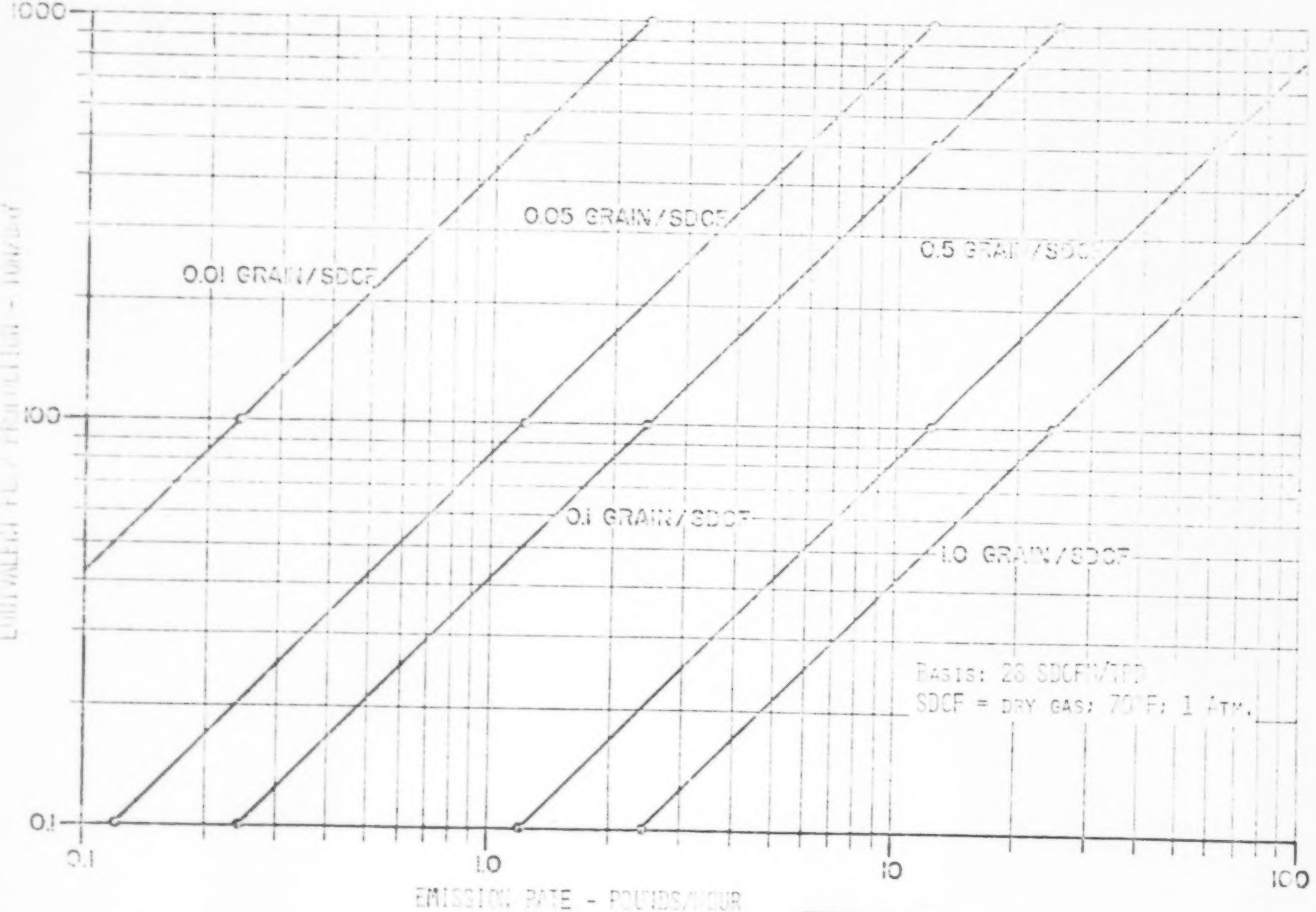


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FIGURE 15. VENT GAS SULFUR CONCENTRATION AND EMISSION RATE RELATIONSHIPS FOR SMELT DISSOLVING TANKS

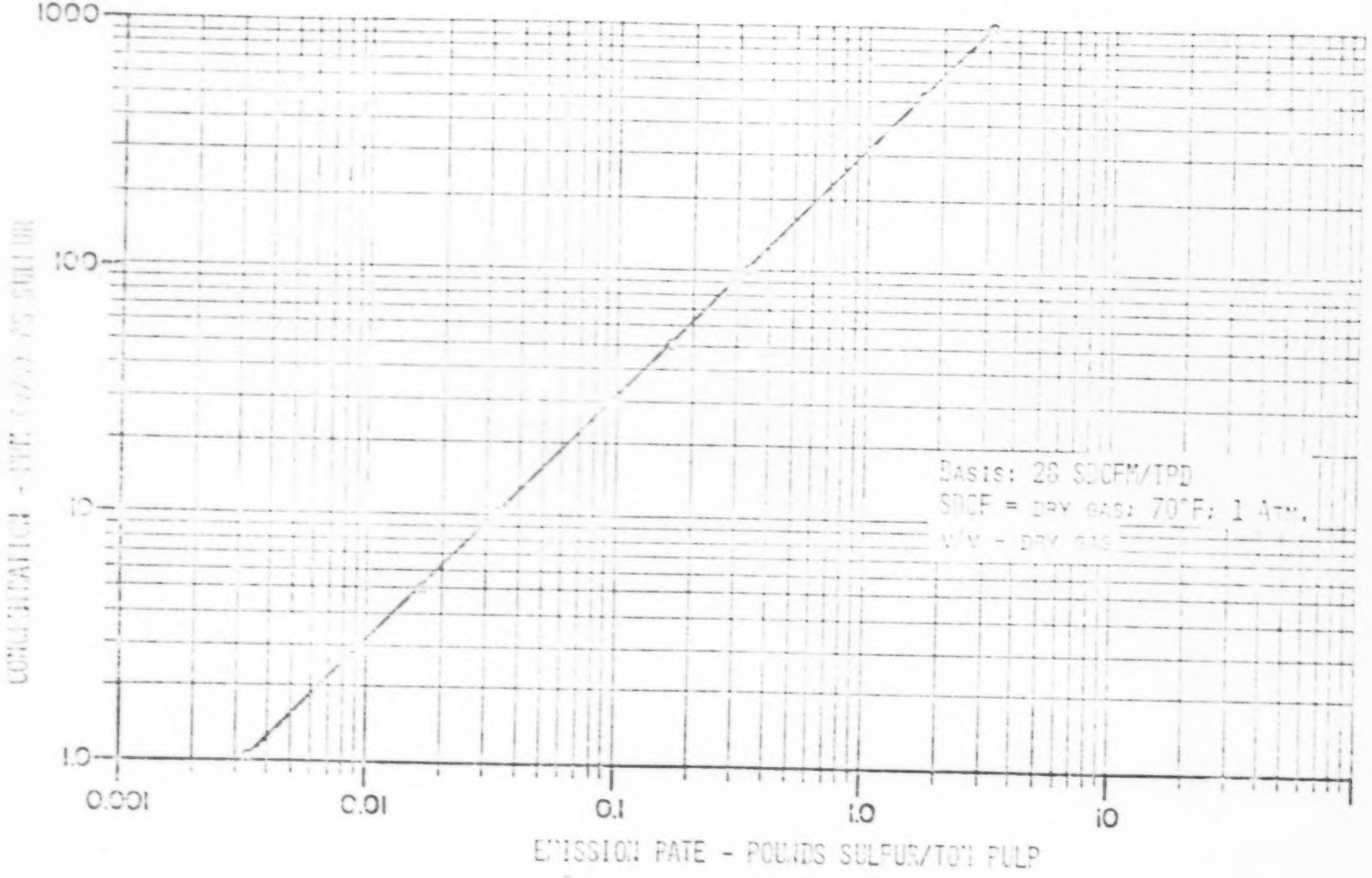
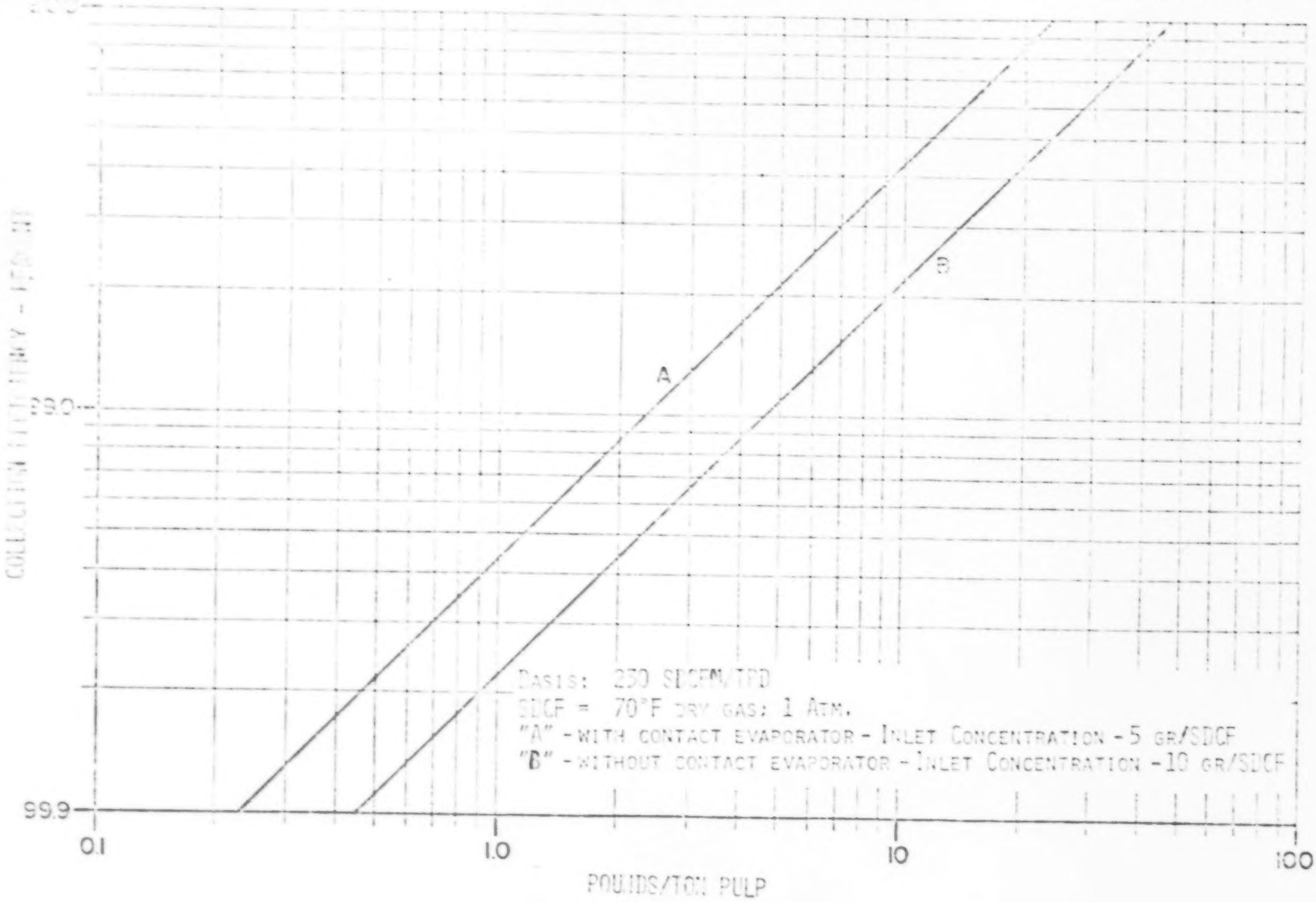


FIGURE 8 - PARTICULATE COLLECTION EFFICIENCY AND EMISSION RATE RELATIONSHIPS FOR KRAFT RECOVERY FURNACES



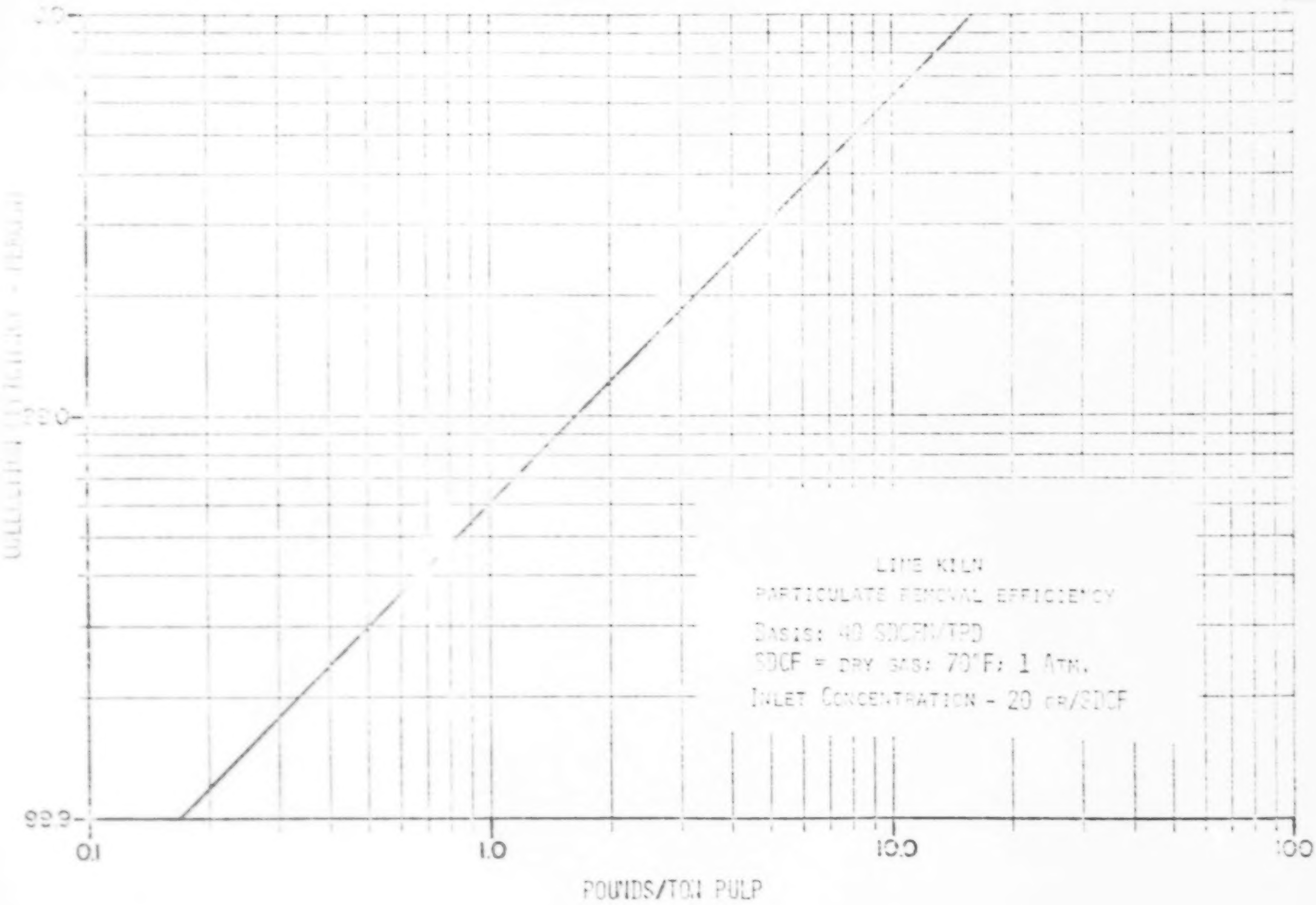
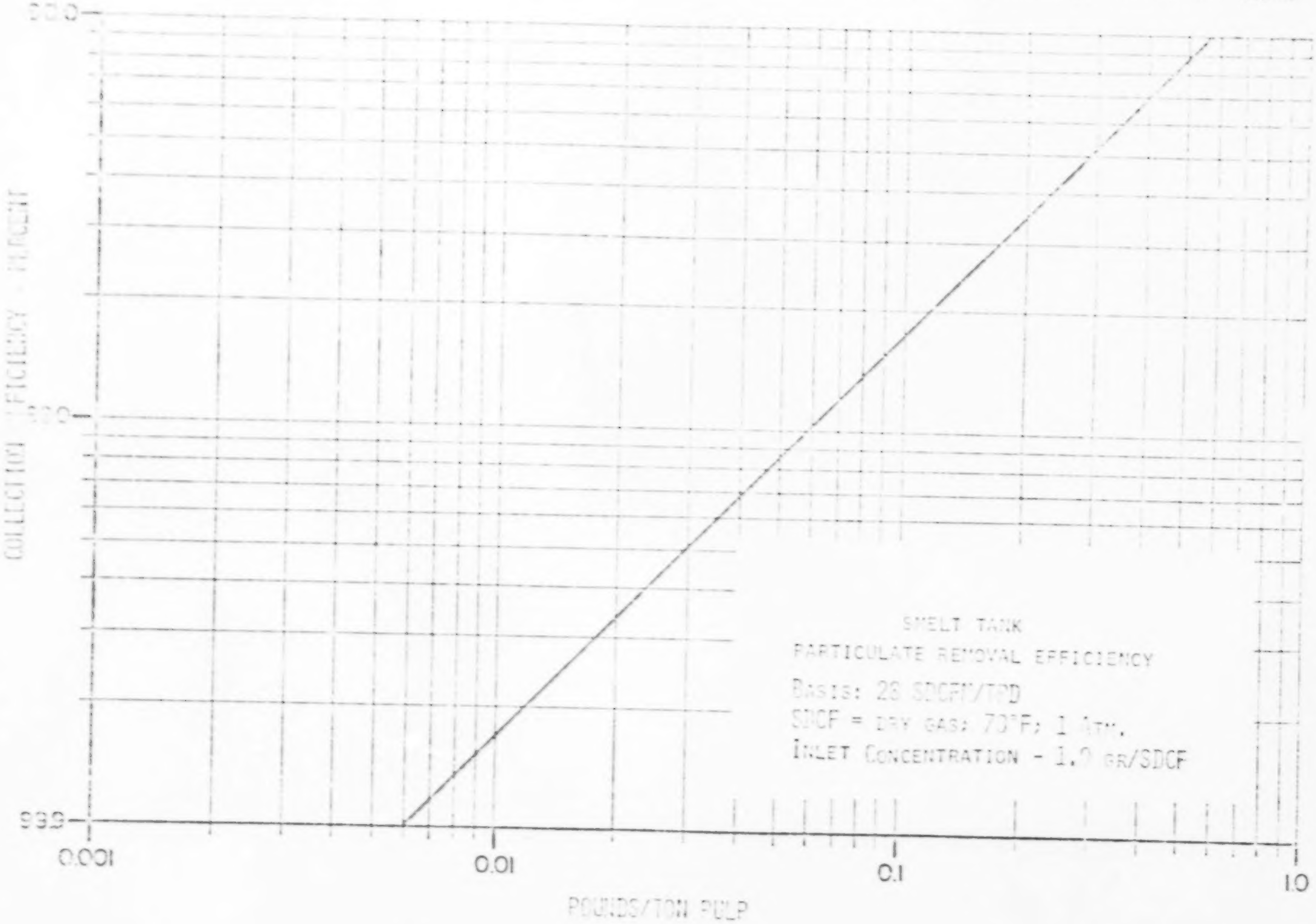

90
99.0
99.9
0.1
1.0
10.0
100
POUNDS/TON PULP
LIME KILN
PARTICULATE REMOVAL EFFICIENCY
BASIS: 40 SDCFM/TPD
SDCF = DRY GAS: 70°F; 1 ATM.
INLET CONCENTRATION - 20 GR/SDCF

FIGURE 18 - PARTICULATE COLLECTION EFFICIENCY AND EMISSION RATE RELATIONSHIPS FOR SMELT DISSOLVING TANKS



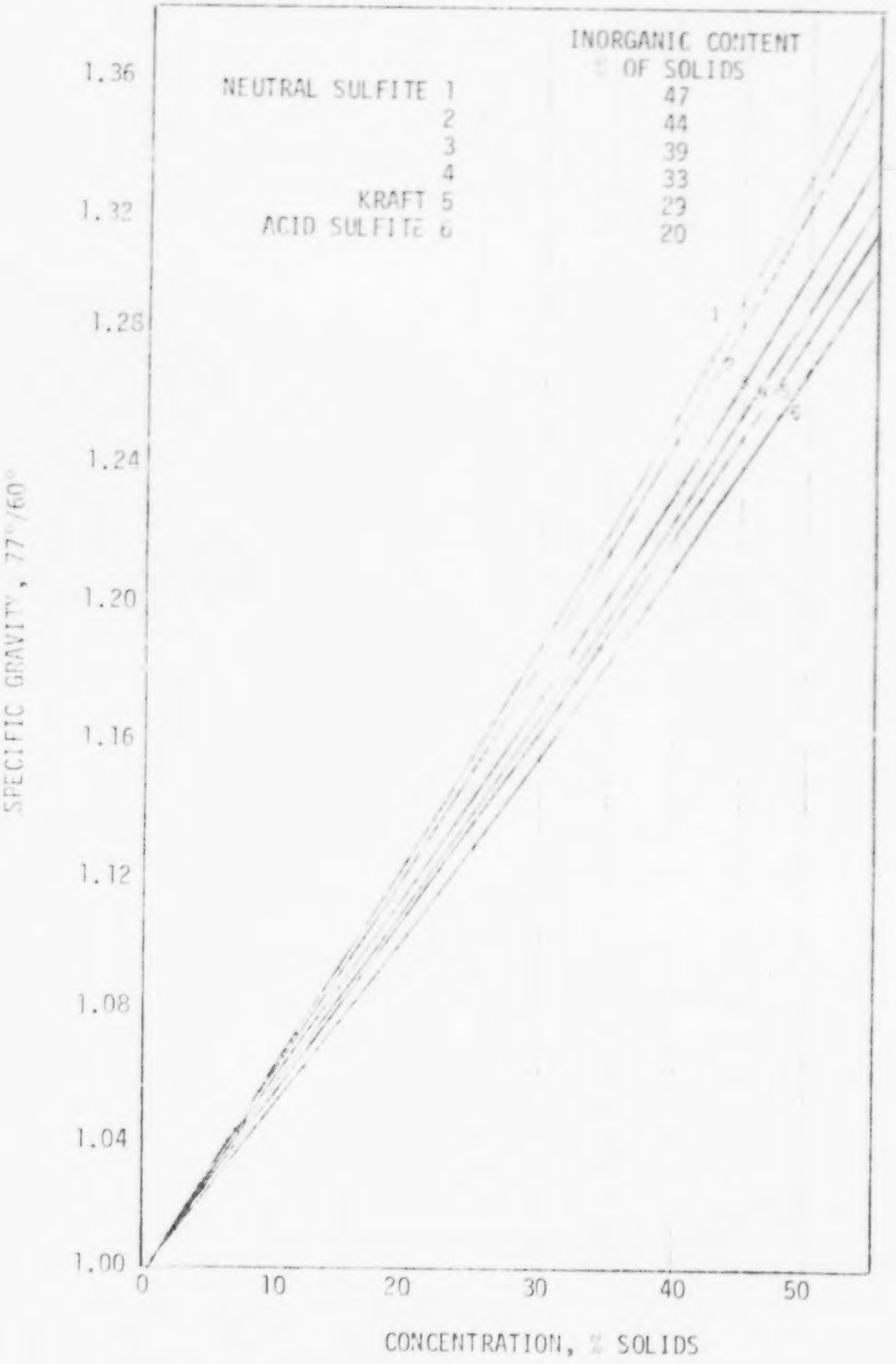


Figure 19. Specific gravity of spent liquors.

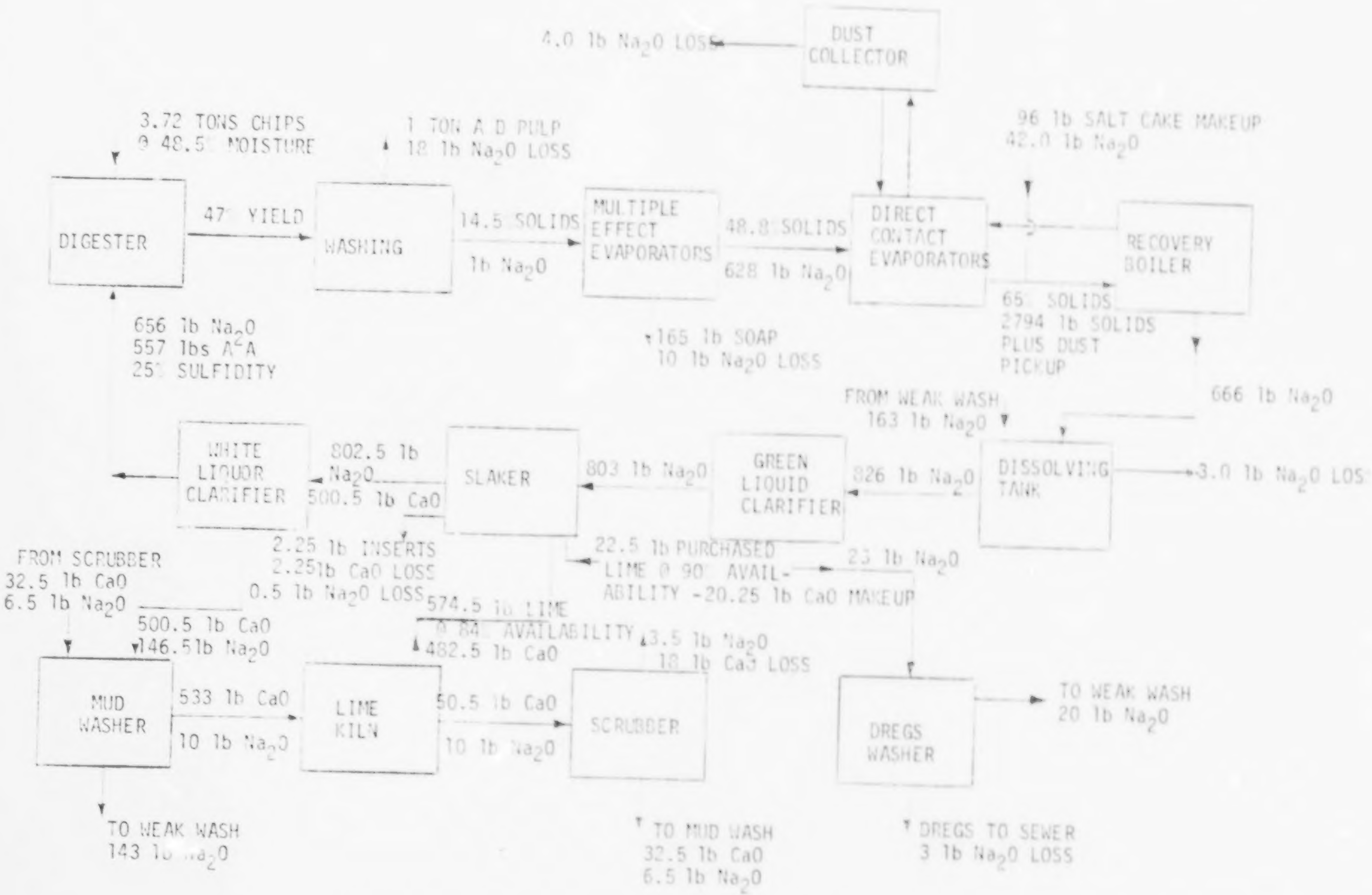

DUST COLLECTOR
4.0 lb Na2O LOSS
3.72 TONS CHIPS
@ 48.5% MOISTURE
1 TON A D PULP
18 lb Na2O LOSS
96 lb SALT CAKE MAKEUP
42.0 lb Na2O
DIGESTER
47% YIELD
WASHING
14.5% SOLIDS
1b Na2O
MULTIPLE EFFECT EVAPORATORS
48.8% SOLIDS
628 lb Na2O
DIRECT CONTACT EVAPORATORS
RECOVERY BOILER
65% SOLIDS
2794 lb SOLIDS
PLUS DUST
PICKUP
656 lb Na2O
557 lbs A2A
25% SULFIDITY
165 lb SOAP
10 lb Na2O LOSS
FROM WEAK WASH
163 lb Na2O
666 lb Na2O
WHITE LIQUOR CLARIFIER
802.5 lb
Na2O
500.5 lb CaO
SLAKER
803 lb Na2O
GREEN LIQUID CLARIFIER
826 lb Na2O
DISSOLVING TANK
3.0 lb Na2O LOSS
2.25 lb INSERTS
2.25lb CaO LOSS
0.5 lb Na2O LOSS
22.5 lb PURCHASED
LIME @ 90% AVAIL-
ABILITY -20.25 lb CaO MAKEUP
23 lb Na2O
FROM SCRUBBER
32.5 lb CaO
6.5 lb Na2O
500.5 lb CaO
146.5lb Na2O
574.5 lb LIME
@ 84% AVAILABILITY
482.5 lb CaO
3.5 lb Na2O
18 lb CaO LOSS
MUD WASHER
533 lb CaO
10 lb Na2O
LIME KILN
50.5 lb CaO
10 lb Na2O
SCRUBBER
DREGS WASHER
TO WEAK WASH
20 lb Na2O
TO WEAK WASH
143 lb Na2O
TO MUD WASH
32.5 lb CaO
6.5 lb Na2O
DREGS TO SEWER
3 lb Na2O LOSS

Figure 20. Chemical balance in recovery cycle.